

Bill Froy

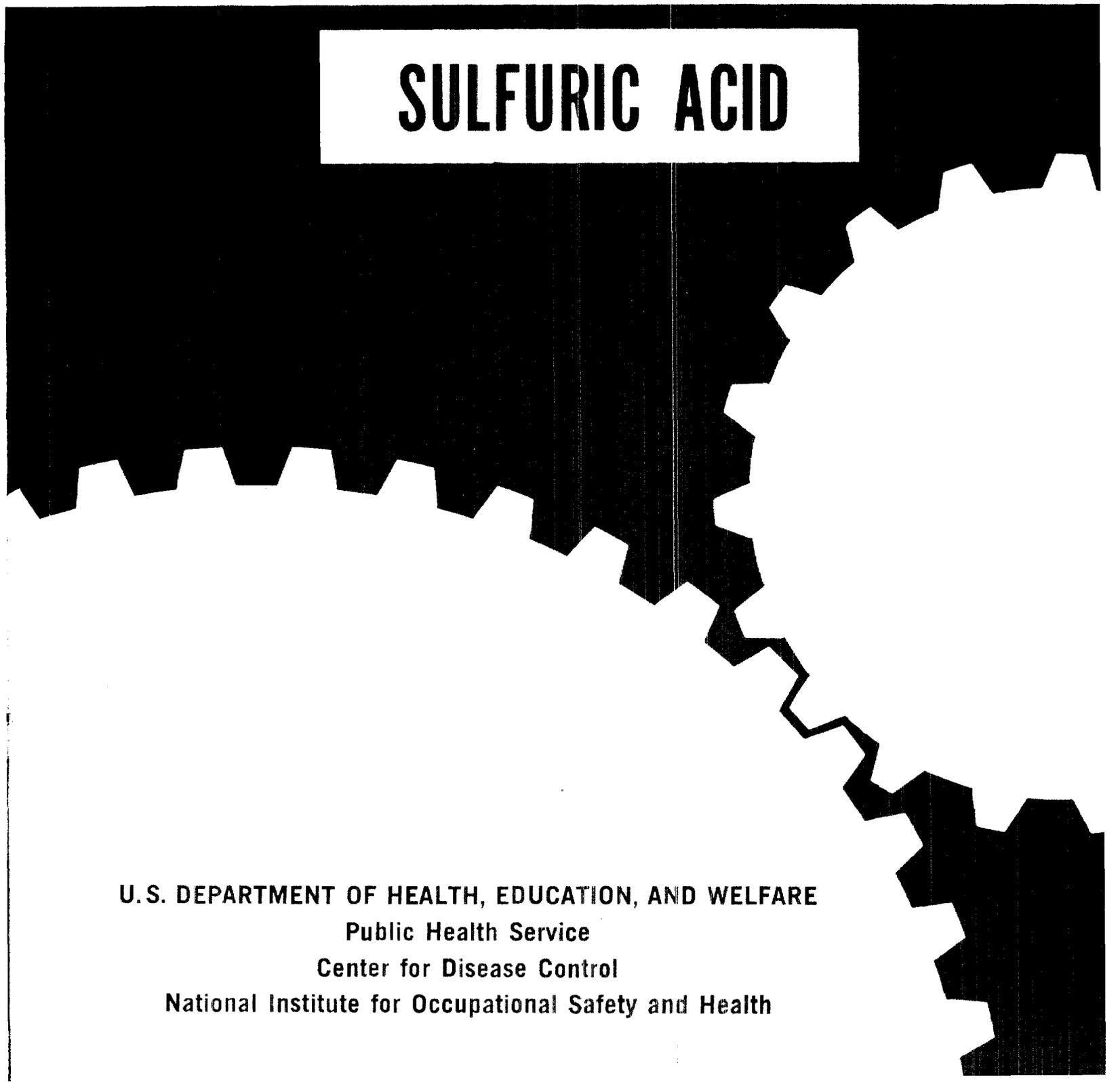
criteria for a recommended standard

OCCUPATIONAL EXPOSURE TO

SULFURIC ACID

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

74-128 H-504



criteria for a recommended standard

**OCCUPATIONAL EXPOSURE
TO
SULFURIC ACID**



U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Center for Disease Control

National Institute for Occupational Safety and Health

1974

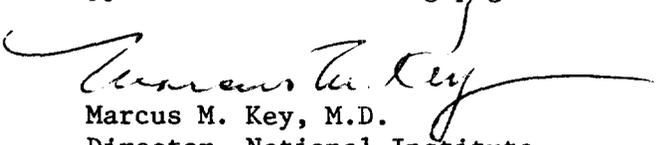
HEW Publication No. (NIOSH) 74-128

PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. To provide relevant data from which valid criteria and effective standards can be deduced, the National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices.

It is intended to present successive reports as research and epidemiologic studies are completed and sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on sulfuric acid by members of my staff, the valuable and constructive comments presented by the Review Consultants on Sulfuric Acid, the ad hoc committees of the Industrial Medical Association and the American Conference of Governmental Industrial Hygienists, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by Professor William A. Burgess, NIOSH consultant on respiratory protection. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on sulfuric acid. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.


Marcus M. Key, M.D.
Director, National Institute
for Occupational Safety and Health

The Office of Research and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for sulfuric acid. Tabershaw-Cooper Associates, Inc., developed the basic information for consideration by NIOSH staff and consultants under contract No. HSM-99-72-116. Douglas L. Smith, Ph.D., served as criteria manager and had NIOSH program responsibility for development of the document.

NIOSH REVIEW CONSULTANTS ON
SULFURIC ACID

William V. Andresen
Director, Occupational Environmental Services
Central Medical Department
American Cyanamid Company
Wayne, New Jersey 07470

Susan M. Daum, M.D.
Department of Community Medicine
Mount Sinai School of Medicine
New York, New York 10029

Howard H. Fawcett
Technical Secretary
Committee on Hazardous Materials
National Research Council
Washington, D.C. 20418

Robert Frank, M.D.
Department of Environmental Health
School of Public Health and Community Medicine
University of Washington
Seattle, Washington 98105

Paul D. Halley
Director, Environmental Health Services Division
Medical and Health Services Department
Standard Oil Company (Indiana)
Chicago, Illinois 60605

Ex Officio:

Keith H. Jacobson, Ph.D.
Office of Research and Standards Development
NIOSH

REVIEW COMMITTEE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Bobby F. Craft, Ph.D.
Director, Division of Technical Services

Russel H. Hendricks, Ph.D.
Division of Laboratories
and Criteria Development

Trent R. Lewis, Ph.D.
Division of Laboratories
and Criteria Development

Frank L. Mitchell, D.O.
Office of Research and
Standards Development

Ruth E. Reifschneider
Division of Technical Services

Edward Shmunis, M.D.
Division of Field Studies
and Clinical Investigations

James B. Walters
Division of Technical Services

Ex Officio:

Herbert E. Christensen, D.Sc.
Acting Deputy Director, Office of
Research and Standards Development

CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN
OCCUPATIONAL EXPOSURE STANDARD FOR SULFURIC ACID

Table of Contents

	<u>Page</u>
PREFACE	
REVIEW COMMITTEES	
I. RECOMMENDATIONS FOR A SULFURIC ACID STANDARD	
Section 1 - Environmental (Workplace Air)	1
Section 2 - Medical	2
Section 3 - Labeling (Posting)	3
Section 4 - Protective Clothing and Personal Protective Equipment	5
Section 5 - Appraisal of Employees of Hazards from Sulfuric Acid	10
Section 6 - Work Practices	11
Section 7 - Monitoring and Reporting Requirements	14
II. INTRODUCTION	17
III. BIOLOGIC EFFECTS OF EXPOSURE	
Extent of Exposure	19
Historical Reports	21
Effects on Humans	22
Epidemiologic Studies	30
Animal Toxicity	38
Correlation of Exposure and Effect	43
IV. ENVIRONMENTAL DATA	
Environmental Concentrations	50
Environmental Sampling and Analytical Method	54
V. DEVELOPMENT OF STANDARD	
Basis for Previous Standards	56
Basis for Recommended Environmental Standard	57

Table of Contents (continued)

VI. WORK PRACTICES	63
VII. REFERENCES	65
VIII. APPENDIX I - Method for Sampling and Analytical Procedures for Determination of Sulfuric Acid	70
IX. APPENDIX II - Material Safety Data Sheet	81
X. TABLES AND FIGURE	82

I. RECOMMENDATIONS FOR A SULFURIC ACID STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to sulfuric acid (H₂SO₄) at the workplace be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for up to a 40-hour work week over a working lifetime; compliance with the standard should therefore prevent adverse effects of sulfuric acid on the health and safety of workers. The standard is measurable by techniques that are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and will be revised as necessary.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Occupational exposure to sulfuric acid mist shall be controlled so that workers shall not be exposed to a concentration greater than one milligram per cubic meter of air (1 mg/cu m) determined as a time-weighted average (TWA) exposure for up to a 10-hour work day, 40-hour work week.

(b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis of environmental samples shall be as provided in Appendix I or by any method

shown to be equivalent in accuracy, precision, and sensitivity to the method specified.

(c) Exposure

"Exposure to sulfuric acid" means exposure to a concentration of liquid, mist, or special dry powder of sulfuric acid, or to sulfur trioxide associated with oleum (fuming sulfuric acid) equal to or above one-half the recommended environmental standard. Exposures at lower environmental concentrations will not require adherence to the following sections except for work practices, equipment, and clothing which may be necessary to guard against the occurrence of foreseeable accidents such as from spray or splash. Procedures for identification of exposure areas can be accomplished by time-weighted average (TWA) determinations by the method described in Appendix I or by any method shown to be equivalent in accuracy, precision, and sensitivity.

Section 2 - Medical

(a) Comprehensive preplacement and annual medical examinations shall be provided for all workers subject to "exposure to sulfuric acid." The examination shall be directed toward, but not limited to, the teeth, eyes, skin, and the cardiopulmonary system. Particular attention shall be focused on dental erosion and complaints of mucous membrane irritation and cough. An evaluation of the advisability of a worker's using negative- or positive-pressure respirators shall also be made.

(b) Initial examinations for presently employed workers shall be offered within 6 months of the promulgation of a standard incorporating these recommendations and annually thereafter.

(c) The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, and of the employer shall have access to all medical records. Physicians designated and authorized by any employee or former employee shall have access to his medical records.

(d) Medical records shall be maintained for persons employed one or more years in work involving exposure to sulfuric acid. X-rays for the 5 years preceding termination of employment and all medical records with pertinent supporting documents shall be maintained at least 20 years after the individual's employment is terminated.

Section 3 - Labeling (Posting)

(a) Areas where sulfuric acid is used, handled, or stored shall be posted with a sign reading:

SULFURIC ACID

Danger! Causes Severe Burns

Do not get in eyes, on skin, on clothing.

Avoid breathing mist.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

Use protective clothing and equipment as instructed.

Do not add water to acid.

UNAUTHORIZED PERSONS KEEP OUT

(b) Areas where oleum (fuming sulfuric acid) is used, handled, or stored shall be posted with a sign reading:

OLEUM

Fuming Sulfuric Acid

Danger! Causes Severe Burns

Do not get in eyes, on skin, on clothing.

Avoid breathing mist or gas.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

Use protective clothing and equipment as instructed.

Do not add water to acid.

UNAUTHORIZED PERSONS KEEP OUT

(c) Areas where bags of dry sulfuric acid are handled or stored shall be posted with a sign reading:

SULFURIC ACID

Dry Sulfuric Acid

Avoid contamination with foreign matter.

Do not rebag contaminated material.

Place broken and torn bags and contents in slipover bags.

Dispose of bags as instructed.

Sweep up and promptly dispose of all spilled material as instructed.

In case of fire avoid use of water directly on bags.

Use protective clothing and equipment as instructed.

UNAUTHORIZED PERSONS KEEP OUT

These signs shall be printed both in English and in the predominant primary language of non-English-speaking workers, if any.

Section 4 - Protective Clothing and Personal Protective Equipment

Engineering controls shall be used to maintain sulfuric acid concentrations below the prescribed limit. Administrative controls may also be used to reduce exposure. Requirements for personal protective equipment shall be as approved under provisions of 29 CFR 1910 (37 FR 22102, Subpart I, October 18, 1972).

(a) Skin Protection

(1) Skin contact with sulfuric acid will produce burns at the site of contact. Impervious protective clothing, such as rubber gloves, aprons, suits, hoods, and boots shall be provided by the employer

and used by the employee as appropriate to the severity and likelihood of body contact with liquid acid.

(2) Sulfuric acid-wetted clothing, unless impervious, shall be removed promptly.

(3) Protective clothing should be changed at least twice a week or more frequently if required.

(b) Eye Protection

Eye protective equipment shall be provided by the employer and used by the employee where eye contact with liquid sulfuric acid is likely.

(1) Selection, use, and maintenance of eye protective equipment shall be in accordance with provisions of the American National Standard Practice for Occupational and Educational Eye and Face Protection, ANSI Z87.1-1968.

(2) Chemical safety goggles-- cup-type, cover-cup-type, or rubber-framed goggles, equipped with approved impact-resistant glass or plastic lenses, shall be worn whenever there is danger of sulfuric acid eye contact.

(3) Face shields-- full length, 8-inch minimum plastic shields with forehead protection may be worn in place of, or in addition to, goggles. If there is danger of material striking the eyes from underneath, or around the sides of the face shield, chemical safety goggles should be worn as added protection.

(c) Respiratory Protection

This subsection shall apply whenever a variance from the standard recommended in Section 1 (a) is granted under provisions of the

Occupational Safety and Health Act, or in the interim period during the application for a variance. When the limits of exposure to sulfuric acid prescribed in subsection (a) of Section 1 cannot be met by controlling the concentration of sulfuric acid in the work environment, an employer must utilize, as provided in this subsection, a program of respiratory protection to effect the required protection of every worker exposed. Respirators shall also be provided and used for nonroutine operations (occasional brief exposures above the TWA of 1 mg/cu m and for emergencies); however, for these instances, a variance is not required, but the requirements set forth below continue to apply. Appropriate respirators as described in Table I-1 shall only be used pursuant to the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure the atmospheric concentration of sulfuric acid in the workplace when the initial application for variance is made and thereafter whenever process, worksite, or climate changes occur which are likely to increase the sulfuric acid concentration. This requirement shall not apply when only atmosphere-supplying positive pressure respirators are used. The employer shall ensure through proper respirator selection, fit, use, and maintenance that no worker is being exposed to sulfuric acid in excess of the standard.

(2) The respirator and cartridge or canister used shall be of the appropriate class, as determined on the basis of exposure to sulfuric acid.

TABLE I-1

REQUIREMENTS FOR RESPIRATOR USAGE

<u>Maximum Use Concentration (Multiples of TWA limit)</u>	<u>Respirator Type (for both sulfuric acid mist and sulfur trioxide unless specified)</u>
Less than or equal to 10x	<p>(1) Type C supplied air respirator, demand type (negative pressure), with quarter, half, or full facepiece; if eye irritation noted, full facepiece must be worn.</p> <p>Sulfur trioxide only--Chemical cartridge respirator for sulfur dioxide with quarter, half, or full facepiece; if eye irritation noted, full facepiece must be worn. Use mist filter when sulfuric acid mist is present.</p> <p>Sulfuric acid mist only--Air purifying mist respirator with cartridge and half mask facepiece; if eye irritation noted, full facepiece must be worn.</p>
Less than or equal to 100x	<p>(1) Gas mask with chin style canister for acid gases and acid mists.</p> <p>(2) Gas mask with front or back mounted chest type canister for acid gases and acid mists.</p> <p>(3) Type C supplied air respirator, demand (negative pressure); pressure-demand; or continuous flow type with full facepiece.</p> <p>(4) Self-contained breathing apparatus in demand mode (negative pressure) with full facepiece.</p>
Greater than 100x	<p>(1) Self-contained breathing apparatus in pressure-demand mode (positive pressure) with full facepiece.</p> <p>(2) Combination supplied air respirator, pressure-demand type, with auxiliary self-contained air supply with full facepiece.</p>

TABLE I-1
(continued)

REQUIREMENTS FOR RESPIRATOR USAGE

<u>Maximum Use Concentration (Multiples of TWA limit)</u>	<u>Respirator Type (for both sulfuric acid mist and sulfur trioxide unless specified)</u>
Emergency (No concentration limit)	(1) Self-contained breathing apparatus in pressure-demand mode (positive pressure) with full facepiece. (2) Combination supplied air respirator, pressure-demand type, with auxiliary self-contained air supply with full facepiece.
Evacuation or escape (No concentration limit)	(1) Self-contained breathing apparatus in demand or pressure-demand mode (negative or positive pressure). (2) Gas mask with acid gas chest canister, and mouthpiece respirator for acid gases and acid mists.

(3) A respiratory protective program meeting the general requirements outlined in Section 3.5 of American National Standard Practices for Respiratory Protection Z88.2-1969 shall be established and enforced by the employer. In addition, Sections 3.6 (Program Administration), 3.7 (Medical Limitations), and 3.8 (Approval) shall be adopted and enforced.

(4) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided.

(5) Respiratory protective devices described in Table I-1 shall be those approved under provisions of 30 CFR 11 (37 FR 6244, March 25, 1972) as amended.

(6) Respirators specified for use in higher concentrations of sulfuric acid are permitted in atmospheres of lower concentrations.

(7) Employees shall be given instruction on the use of respirators assigned to them, day-to-day maintenance and cleaning of the respirators, and how to test for leakage.

(8) Emergency and escape-type respirators shall be made immediately available at the work stations for each worker.

Section 5 - Appraisal of Employees of Hazards from Sulfuric Acid

At the beginning of employment in a sulfuric acid area, employees exposed to sulfuric acid shall be informed of all hazards, relevant symptoms of overexposure, appropriate emergency procedures, and proper conditions and precautions for safe use or exposure. The information shall be posted in the work area and kept on file and readily accessible to the worker at all places of employment where sulfuric acid is involved in unit processes and operations or is released as a product, byproduct, or contaminant.

A continuing educational program shall be instituted to ensure that all workers have current knowledge of job hazards, proper maintenance procedures and cleanup methods, and that they know how to correctly use respiratory protective equipment and protective clothing.

Information as required shall be recorded on US Department of Labor Form OSHA-20 "Material Safety Data Sheet" or a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

Emphasis shall be placed upon handling, cleanup, inspection and repair of equipment and leaks, storage, and proper disposal of materials.

(a) Handling

(1) Transfer of sulfuric acid from one container to another, or into any process, shall be performed in such a manner as to prevent spillage or leakage. The safe handling practices for sulfuric acid described in Sulfuric Acid, Use and Handling by Fasullo, 1965, are recommended.

(2) Carboys and drums of sulfuric acid should be emptied by gravity or by siphon--never by pressure. Employees opening such containers should wear approved impervious clothing, goggles, face shields, and rubber gloves.

(3) If it is necessary to enter an uncleaned, enclosed tank which has contained sulfuric acid, workers shall be equipped with hood-type face shields or goggles, impervious clothes, rubber safety toe-cap shoes, rubber gloves, brimmed felt or treated fiber hats, and self-contained or supplied air respiratory protective equipment.

(4) If acid is to be diluted with water, the acid shall be added to the water except that in special cases when water must be added to acid, suitable precautions shall be taken.

(b) Emergency, Cleanup, and Inspection

(1) Procedures for emergencies shall be established to meet foreseeable events. The irritant and corrosive properties of sulfuric acid demand that corrective measures be instituted as soon as possible.

(2) In the event of spills or leaks, sulfuric acid shall be neutralized with soda ash (sodium carbonate), washing soda, or suitable material and washed down with copious amounts of water. The contaminated area shall be immediately zoned off and ventilated thoroughly.

(3) Where there is the possibility of sulfuric acid contact on the eyes or skin, safety showers, eye-wash fountains, and cleansing facilities shall be installed and maintained to provide prompt, immediate access by the workers. The safety showers should have quick-acting valves and deluge-type heads. Inspections and tests shall be conducted at least every 30 days to ensure proper operation.

(4) Appropriate respirators shall be immediately available for wear during evacuation.

(5) Each shipment of sulfuric acid shall be inspected for leakage upon arrival or upon transfer or filling operations. Pipelines, equipment, and containers shall be examined periodically for leaks at least every 3 months.

(c) Exhaust Systems and Enclosure

(1) Exhaust ventilation and enclosure processes shall be used wherever practicable to control workplace concentrations. Systems

shall be designed and maintained to prevent the accumulation or recirculation of sulfuric acid into the workplace.

(2) Ventilation, enclosure, surface active agents, chips, etc, shall be used where operations or processes result in the evolution of sulfuric acid so as to protect employees from airborne concentrations in excess of the requirements of Section 1 (a) of the Standard. It is also necessary to remove hazardous concentrations of toxic gases such as arsine or hydrogen selenide which may result from the interaction of hydrogen with impurities present either in sulfuric acid or in metals with which the acid comes in contact.

(d) Storage

(1) Sulfuric acid shall be isolated from organic materials, nitrates, carbides, chlorates, chromates, cyanides, metallic sulfides, and metal powders or other noncompatible materials because contact with these materials may cause evolution of toxic gases and/or ignition. Storage shall be on separate, well ventilated, cool, dry premises.

(2) Smoking, open lights, flames, and spark-producing tools shall not be permitted near sulfuric acid carboys, drums, tank cars, or metal storage tanks because of the possible production of explosive mixtures of hydrogen during storage.

(e) Disposal

(1) All local, state, and federal regulations concerning waste disposal into landfills, streams, municipal treatment plants, or impounding basins shall be followed.

Section 7 - Monitoring and Reporting Requirements

Workroom areas where it has been determined, on the basis of an industrial hygiene survey or the judgment of a compliance officer, that environmental levels do not exceed half the environmental standard shall not be considered to have sulfuric acid exposure. Records of these surveys, including the basis for concluding that air levels are not above half the environmental standard, shall be maintained until a new survey is conducted. Surveys shall be repeated when any process change indicates a need for reevaluation or at the discretion of the compliance officer. Requirements set forth below apply to areas in which there is sulfuric acid exposure.

Employers shall maintain records of accidental sulfuric acid release requiring evacuation. In addition, records of environmental exposures to sulfuric acid shall be maintained based upon the following sampling and recording schedules except as otherwise indicated by a professional industrial hygiene survey. In all monitoring, samples representative of the exposure in the breathing zone of employees shall be collected. An adequate number of samples shall be collected to permit construction of a time-weighted average (TWA) exposure for every operation or process. The minimum number of representative TWA determinations for an operation or process shall be based on the number of workers exposed as provided in Table I-2.

(a) Initial and Recurrent Sampling Procedures

(1) The first environmental sampling shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(2) Samples shall be collected at least semiannually in accordance with Appendix I for the evaluation of the work environment with respect to the recommended standard.

(b) Special Sampling Procedures

(1) Environmental monitoring of an operation or process shall be repeated at 15-day intervals when the sulfuric acid concentrations have been found to exceed the recommended environmental standard. In such cases, suitable controls shall be initiated, and monitoring shall continue at 15-day intervals until two consecutive surveys indicate the adequacy of the controls.

(2) Environmental samples shall be taken within 30 days after installation of a new process or process change.

(c) Recordkeeping Procedures

(1) Records of all sampling and medical examinations shall be maintained for at least 20 years after the individual's employment is terminated. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Records shall be maintained so that they can be classified by employee. Each employee shall be able to obtain information on his own environmental exposure.

TABLE I-2
SAMPLING SCHEDULE

<u>Number of Employees Exposed</u>	<u>Number of TWA Determinations</u>
1-20	50% of the total number of workers
21-100	10 plus 25% of the excess over 20 workers
over 100	30 plus 5% of the excess over 100 workers

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to sulfuric acid. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe... exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultations with others, has formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. It should be pointed out that any recommended criteria for a standard should enable management and labor to develop better engineering controls resulting in more healthful work practices and should not be used as a final goal.

These criteria for a standard for sulfuric acid are part of a continuing series of criteria developed by NIOSH. The proposed standard applies to the processing, manufacture, and use of sulfuric acid, or its release as an intermediate, byproduct, or impurity as applicable under the Occupational Safety and Health Act of 1970.

These criteria were developed to ensure that the standard based thereon would (1) protect against development of acute and chronic sulfuric acid poisoning, (2) be measurable by techniques that are valid, reproducible, and available to industry and governmental agencies, and (3) be attainable with existing technology.

From the health hazard standpoint, sulfuric acid must be handled with utmost care because of its highly corrosive action on the skin, eyes, and respiratory tract. The importance of good work practices is emphasized herein, along with the necessary documentation from which the proposed environmental standard is recommended. In addition, it is recognized that a great potential hazard exists, particularly by inhalation, from the use of oleum (fuming sulfuric acid).

These criteria were not designed for the population-at-large and any extrapolation beyond general occupational exposures is not warranted.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Sulfuric acid is produced by the oxidation of sulfur dioxide. [1] Approximately 99% of all production is now by the contact process. It is one of the most widely used chemical compounds.

Sulfuric acid is a colorless to cloudy liquid. Fuming sulfuric acid (oleum) has a sharp, penetrating odor. Concentrated sulfuric acid has an extremely irritant, corrosive, and destructive action on all living matter, including human tissues, not by virtue of its acidity (in concentrated form it is only slightly ionized) but because of its affinity for water. The affinity is so strong that it will remove the elements of water from even anhydrous organic matter such as carbohydrates, resulting in charring or carbonization with the liberation of heat. In sulfuric acid splashing accidents, the heat liberated by dilution of the concentrated acid with water used to flush the affected areas, can add thermal burn to chemical injury of the body.

Oleum, or fuming sulfuric acid, is a solution of sulfuric anhydride (sulfur trioxide) in anhydrous sulfuric acid. The "fumes" of oleum are initially composed of sulfur trioxide which will combine with water, either present in the air or on the mucous membranes of exposed persons, to form sulfuric acid. Effectively then, exposure to sulfur trioxide is equivalent to exposure to sulfuric acid, the site of effect in the respiratory tract being largely determined by droplet size. [2] The more important strengths, properties, and characteristics of sulfuric acid and oleum are presented in Table X-1. [3]

Sulfuric acid mist, the airborne form of sulfuric acid, is an aerosol of droplets of varying diameter of aqueous sulfuric acid solution, the concentration of which will initially depend upon the concentrations of the liquid acid from which the mist is generated. However, the concentration of droplets may change as the highly hygroscopic droplets pick up more water from the atmosphere, growing in size in the process. Sulfate is one of the normal anions in the body [4]; however, the occupational hazard results not from the sulfate ion, but it is related either to the hygroscopic characteristics of the acid or to its oxidizing potential.

Among the common processes which result in the evolution of sulfuric acid mist are pickling, anodizing, and plate-forming and charging in battery manufacturing. Exposures to the mist may result whenever sulfuric acid is heated in the open air or when gas bubbles are released from a liquid surface containing the acid.

Table X-2 [5] indicates the important uses of sulfuric acid and Table X-3 [6] lists representative occupations with potential exposures to sulfuric acid. It is an active acid, with catalytic properties, a special affinity for water, and a high boiling point. Such properties, together with its low cost, make it useful for many purposes. Among these are the pickling of steel, the manufacture of halogen acids, removal of water vapor from gases, alkylation operations in the petroleum and petrochemical industries, acidulation and neutralization processes, and the manufacture of organic sulfonates used in household detergents and lubricants. The single largest use of sulfuric acid is in the manufacture

of phosphate fertilizers. [5] Sulfuric acid production in the United States in 1970 was almost 30 million tons. [7]

A small amount of sulfuric acid is available in a "dry" powdered form, composed of 80% by weight of 1.835 specific gravity sulfuric acid and 20% inert absorbent material (synthetic hydrated silicate). The particle size of the powder is approximately 0.02 to 0.07 μm . In use, the powder is dissolved in water and filtered, yielding a clear acid in strengths up to 60%. [8]

NIOSH estimates that 200,000 persons in the work force have potential exposure to sulfuric acid.

Historical Reports

Alfred Nobel, prior to the establishment of the Nobel awards, is said to have commented that the economic progress of a country might be measured in terms of how much sulfuric acid is consumed through manufacturing productivity. In view of the 200 years history of the use of sulfuric acid in industry [9] and the wide variety of industries in which it has been used, there is a remarkable dearth of reports in the early literature concerning adverse health effects of sulfuric acid in any form, including mist. Possibly the effects of concentrated sulfuric acid splashed on the skin or eyes are too well known for published comment. [10]

Greenwald [11] in 1954 reviewed occupational and experimental observations of exposure to sulfuric acid mist in conjunction with

his review of the effects of sulfur dioxide exposure upon man and animals. Dorsch [12] in 1913 presented the only historical report of adverse health effects in workers to sulfuric acid mist. He noted coughing and sneezing among exposed persons in a lead-sulfuric acid battery room of a telephone exchange. Dorsch [12] also made the following observations on himself and his colleagues: below 0.5 mg/cu m (expressed as SO₂), hardly noticeable "annoyance"; between 0.5 and 2 mg/cu m, slight, from 3 to 4 mg/cu m, distinct; and from 6 to 8 mg/cu m, strong "annoyance" or "nuisance." He also personally experienced nosebleeds on occasions when exposed in the 3.12 to 8.3 mg/cu m range (again expressed as SO₂). Values would be approximately 50% greater if they were calculated as sulfuric acid.

Although there is evidence, both circumstantial and direct, that sulfuric acid aerosol was a significant atmospheric pollutant in some instances of "smog" episodes in the population-at-large, [13] many other factors have undoubtedly also been present.

Effects on Humans

(a) Observed Effects

Concentrated sulfuric acid, by virtue of its great affinity and strong exothermic reaction with water, will effectively remove the elements of water from many organic materials with which it comes in contact, thus it can burn and char the skin. [9] It is even more rapidly injurious to the mucous membranes, and exceedingly dangerous to the eyes. Dilute sulfuric acid, while it does not possess this

charring property, irritates the skin and mucous membranes by virtue of its acidity and can cause dermatitis. [10]

Splash injuries to the eyes are in practice the most serious adverse health effect of sulfuric acid in industry, because contact with concentrated acid of any magnitude is capable of causing irreparable corneal damage resulting in blindness. [5] At the same time, acid burns of the eyelids and surrounding parts of the face will produce cicatrization with disfigurement. [14]

As liquid sulfuric acid becomes progressively more dilute with water, the intensity of its dehydration/charring action gradually diminishes and it then behaves as a strong mineral acid by virtue of its complete ionization. Oleum, or fuming sulfuric acid, may be regarded as sulfuric acid of above 100% concentration, because it contains sulfur trioxide (sulfuric anhydride) in solution. As oleum combines with water, more sulfuric acid is formed until all the sulfur trioxide is consumed. Only thereafter does the sulfuric acid start to become diluted. [5]

The effects of exposure to mist of sulfuric acid in the human can be considered under two distinct headings: irritant effects on the mucous membranes, including those of the eyes, but principally the respiratory tract epithelium, [15, 16, 17, 18] and the chemical corrosive effects upon the teeth. [19, 20]

Exposure to sulfuric acid at the mist concentrations encountered in certain industries [20] (about 0.8 to 17 mg/cu m and sometimes higher) causes first, etching of the dental enamel, and then erosion of enamel and dentine with loss of tooth substance. The damage is limited to the parts

of the teeth which are exposed to direct impingement of acid mist droplets upon the surface. [19,20] This phenomenon does not seem to influence dental caries or other dental and periodontal lesions. The teeth affected are mostly the central and lateral incisors, and, to a much less extent, both the upper and lower canines. The observed effects are largely influenced by the degree of mouth-breathing and by the resting position of the lips, which effectively shield the teeth from the acid. In severe cases, which usually develop after many years of exposure, the loss of tooth substance may cause considerable cosmetic disfigurement as well as functional loss due to nonapposition of the cutting teeth. Denuding of the dentine may make the teeth sensitive to temperature extremes. [19]

Inhalation of sulfuric acid in high enough concentration causes an irritation or tickling of the nose and throat, sneezing, and coughing which is somewhat likened to the effects of breathing dusty air. At levels below those detectable by the foregoing subjective effects, sulfuric acid causes a reflex increase in the rate, and diminution of the depth, of respiration, [16] with reflex bronchoconstriction resulting in increased pulmonary air flow resistance. [17] Exposure to higher concentrations or for longer periods may result in bronchitic symptoms, [17, 21] and rhinorrhea, lacrimation, and epistaxis. [16] Over the course of many years, exposure to sulfuric acid has also been claimed to result in conjunctivitis, frequent respiratory infections, emphysema, and digestive disturbances. [21] However, other substances, including dusts, have also been associated with the effects noted. A single overexposure to sulfuric acid may lead acutely

to laryngeal, tracheobronchial, and even pulmonary edema, and chronically to pulmonary fibrosis, residual bronchiectasis, and pulmonary emphysema. [14]

Dilute sulfuric acid, as with sulfuric acid mist, is absorbed as sulfate and hydrogen ions through mucous membranes, ultimately into the bloodstream. The sulfate ion is quite stable in the body and one of the normal minor anions of the plasma. Some sulfate (6 to 8%) from the plasma pool is conjugated in the liver with such metabolites as phenol, cresol, indole, and skatole and excreted in the urine as "ethereal sulfates." Such urinary excretion of the ethereal sulfates constitutes a detoxicating mechanism. The inorganic sulfate (85 to 90%) is excreted as compounds of sulfuric acid with Na, K, Ca, and NH₃. The remainder, neutral sulfur (4 to 6%), is excreted in compounds such as sulfur-containing amino acids, thiosulfates, and thiocyanates. [22]

There is some evidence that acclimatization to the subjective effects of inhalation of sulfuric acid mist may occur in many persons who are occupationally exposed, to the extent that they may be able to tolerate 3 or 4 times the exposure levels which are intolerable to the unacclimated. [23] On the other hand, there is also limited, inadequate evidence that sensitization to the effects of sulfuric acid mist may occur. [17] Possibly both phenomena occur, and in the industrial situation, self-selection may take place. Individuals becoming acclimatized would most likely remain in an occupation involving exposure to sulfuric acid mist, whereas those with either an idiosyncratic hypersusceptibility or an acquired hypersensitivity leave such employment.

Bushtueva [24] failed to find any evidence of potentiation between sulfuric acid aerosol at 0.3 mg/cu m and 0.7 mg/cu m and sulfur dioxide at 0.65 and 3 mg/cu m, respectively, to effects on the light sensitivity of the dark adapted eye in 3 women subjects. The simultaneous administration of 0.3 mg/cu m sulfuric acid and 0.65 mg/cu m sulfur dioxide failed to produce an effect which differed from unexposed control determinations. The combination of 0.7 mg/cu m sulfuric acid and 3 mg/cu m sulfur dioxide produced simple physiological summation of effects as compared with effects produced by each substance separately. Similarly, the percent prolongation of the time required to produce a reflex optical stimulus (optical chronaxy) was also reported to be simply additive for a combination of 0.73 mg/cu m sulfuric acid and 1.5 mg/cu m sulfur dioxide. On the other hand, Amdur in 1954 [25] demonstrated potentiation between sulfuric acid and sulfur dioxide in guinea pigs with respect to growth, lung changes, and respiratory alterations (see Animal Toxicity).

(b) Human Experimental

In the past two decades a certain amount of human as well as animal experimental work has been performed with sulfuric acid aerosols, some of it at exposure levels relevant to the occupational situation, that is, in the 0.35 to 40 mg/cu m range.

In 1952, Amdur and her associates [16] reported exposing by mask a group of 15 normal subjects, men and women, to levels of 0.35 to 5 mg/cu m sulfuric acid aerosol (1.0 μ m mean particle size), for periods of 5 to 15 minutes and determined subjective sensations, percent

retention of sulfuric acid, and respiratory effects from pneumotachygraph tracings indicating rate and depth of respiration. Their results are tabulated as follows:

<u>Concentration mg H₂SO₄/cu m</u>	<u>Subjective Effects</u>	<u>Respiratory Effects</u>
0.35	Not detected	Increased rate in 5 subjects
0.40	Not detected	Increased rate in 5 others
0.50	Not detected	Increased rate in remaining 5 subjects
1.0	Detected by 2 subjects	Increased rate, forced expiration in 1 subject
2.0	Not reported	Increased rate more rapid and marked, recovery slower
3.0	Detected by all	
5.0	Very objectionable to some but less so to others; usually caused cough	More marked and varied effects on respiratory rate

The increase in rate of respiration was always accompanied by some decrease in depth and also by a decrease in maximum inspiratory and expiratory flow rates. Retention of sulfuric acid in the respiratory tract averaged 77% over a 0.4 to 1.0 mg/cu m exposure concentration range.

Morando, [26] in 1956 reported surprisingly similar information to that given by Amdur et al [16] which indicated that Morando was probably presenting data as exemplary of the effects resulting from exposures to low concentrations of sulfuric acid in humans under experimental conditions.

In 1957, Sim and Pattle [17] exposed healthy male volunteers by mask to 10 N acid mist concentrations ranging from 3 to 39 mg/cu m (1 μ m median diameter) at 62% relative humidity. The subjects were also exposed in a chamber to 4 N acid mist of from 11.5 to 38 mg/cu m (1.5 μ m median diameter) at 91% relative humidity. Mask exposures were of 10 minutes' duration and chamber exposures were up to 60 minutes in duration. In general, the sulfuric acid was much more irritating at higher humidity. The irritant effect of 20.8 mg sulfuric acid/cu m at high humidity (and larger particle size) was greater than that of 39.4 mg sulfuric acid/cu m at lower humidity (and smaller particle size). Under the conditions of high humidity, increases in airway resistance of from 43 to 150% above preexposure levels were measured and increases under the lower humidity conditions (62%) ranged from 35.5 to 100%.

A study on pulmonary airway resistance by Toyama and Nakamura in 1964 [27] reported interaction between hydrogen peroxide aerosols and sulfur dioxide. The interaction product was reported as sulfuric acid aerosol. Nine healthy male volunteers were exposed, through mouth breathing, to reported concentrations of from 0.01 to 0.1 mg/cu m sulfuric acid of 1.8 μ m "count median diameter" (CMD) for a period of 5 minutes. Fifteen similar subjects were reportedly exposed to from 0.8 to 1.4 mg/cu m sulfuric acid of 4.6 μ m CMD. Both exposures followed in sequence 5 minutes' exposure to similar aerosols of hydrogen peroxide alone, and 5 minutes' exposure to 1 to 60 ppm sulfur dioxide alone. The sulfuric acid exposures represented simultaneous administration of predetermined amounts of the hydrogen peroxide and sulfur dioxide.

Airway resistance was measured by an airflow interruption technique. Airway resistance was not statistically different from controls by inhalation of hydrogen peroxide aerosol alone, it was increased following inhalation of sulfur dioxide alone to an extent partly dependent upon concentration, and the airway resistance was increased more on exposure to sulfuric acid mist (hydrogen peroxide and sulfur dioxide together). The mean increase in airway resistance was 36.5% above preexposure baseline in the 15 subjects exposed to the higher sulfuric acid concentration and larger droplets (4.6 μm CMD). The mean increase in airway resistance in the 9 subjects exposed to the lower concentration and smaller droplets was 17.9%. Considerable individual variation existed in sensitivity to change in airway resistance. Furthermore, no data were given concerning how much unreacted sulfur dioxide or hydrogen peroxide was present during the sulfuric acid exposure phases of the study.

Bushtueva in 1957 [18] exposed 10 human subjects to low concentrations of sulfuric acid aerosol to determine the subjective threshold for irritation and other low level effects. The mean minimum concentration was 0.72 mg/cu m (range, 0.6 to 0.85 mg/cu m) to which the 10 subjects, averaging 33 tests per subject, detected minimal effects of throat tickling and scratching. At 1.1 to 2.4 mg/cu m, all subjects noticed considerable irritation at the base of the esophagus and 40% of the subjects noticed irritation of the eyes. At 2.4 to 6.0 mg/cu m, all subjects experienced acute irritation of the mucous membranes and a

pronounced reflex cough. All individuals experienced eye irritation at this exposure level. Pneumographic studies were performed on three of the subjects exposed to 0.6 to 2.0 mg/cu m. No respiratory changes were elicited by exposures to less than 1.0 mg/cu m. Slight changes in respiration occurred at levels of 1.0 to 1.1 mg/cu m and concentrations of 1.8 to 2.0 mg/cu m produced changes in respiratory amplitude and rhythm in all subjects. The particle size of the mists and the ambient humidity were not given.

Bushtueva [24] also studied sensory and central nervous system responses to sulfuric acid mist with and without sulfur dioxide in female volunteer subjects. The effects studied were optical chronaxy (in 1 subject) and dark adaptation (in 3 subjects). A sulfuric acid concentration of 0.73 mg/cu m was reported to elicit a threshold response, an approximately 19% prolongation of chronaxy, whereas 0.6 mg/cu m sulfuric acid was subthreshold. Similarly, 0.7 mg/cu m sulfuric acid produced an average 24% increase above control levels in sensitivity to light during the dark adaptation studies. A sulfuric acid concentration of 0.3 mg/cu m was below the sensitivity thresholds of the test subjects. Sulfuric acid aerosols given in combination with sulfur dioxide resulted in simple addition of physiological effects (see Effects on Humans).

Epidemiologic Studies

Very few epidemiologic studies of health effects resulting from sulfuric acid exposure have been carried out in industry. In recent

years, there have been some community studies of morbidity and mortality associated with "smog" episodes, but since sulfuric acid is only one of the significant constituents of most smogs, the results of such studies have little meaning to the industrial sulfuric acid exposure situation.

In 1970, Williams [28] studied sickness absence and ventilatory capacity in 461 workers exposed to sulfuric acid mist in the manufacture of lead-acid batteries. Sickness absence rates, expressed as spells of sickness per man-year of exposure, were compared in plate-forming workers who were exposed to sulfuric acid mist with workers unexposed to acid who served as controls and who worked in the pasting and assembly departments of the same battery plant. The respective sickness absence records of 157 ex-workers in plate-forming and assembly departments, prior to their leaving employment, was also determined for comparison purposes. No environmental measurements of sulfuric acid levels were made expressly for this study. Two estimates were obtained from separate environmental investigations in the same plant. One of these (3 to 16.6 mg/cu m) was obtained from determinations obtained on a single day within the epidemiologic study period, 1950-1962. [20] The second estimate was made 6 years after the end of the study and was reported as 1.4 mg/cu m (mean) with a range from 0.2 to 5.6 mg/cu m. [29] Ventilatory capacity measurements, forced vital capacity (FVC) and forced expiratory volume in the first second (FEV 1), were conducted on 29 forming workers (exposed group) and 16 plate-cutting workers (controls) at the beginning and end of the work shifts on Monday and Friday.

For all respiratory diseases, classified according to the International Classification of Diseases, [30] both younger (20 to 34 years) and older (35 to 64 years) forming workers and ex-workers had more spells of sickness absence than was expected from a calculated rate of all men. Pasting and assembly workers (controls) had fewer spells than expected. It was suggested that the increased number of spells of respiratory diseases in men exposed to sulfuric acid mist was due to an increased incidence of spells in attacked men rather than by an increased proportion of men attacked. No tests of statistical significance were made because of the variation in the number of spells of sickness absence which was contributed by different individuals. Both exposed and control workers showed a statistically significant decrease in mean FVC and FEV 1 during both Monday and Friday shifts. These decreases were somewhat larger in the exposed than in the control groups but the author considered this difference to be insignificant and attributed the decrease in both groups to circadian (presumably day-night) variation. It was suggested that the absence of statistically significant differences in FVC and FEV 1 between the exposed and control groups could have been due to the several minutes which elapsed between exposure to acid mist and observations of ventilatory capacity in the medical department. It was concluded from the study that an excess of spells of respiratory disease, especially bronchitis, occurred in the forming group. It seemed likely that there were one or more factors present in the forming operation which was

specifically associated with bronchitis and other respiratory disease in susceptible individuals. It was also suggested by Williams [28] that the absence of any considerable lower respiratory tract disease observed in this study might be due to the large size of the mist particles or droplets, thus preventing their reaching the deep lung. Although the mist particle size was not measured in this plant, it was found in the forming department of another similar factory to have a mass median diameter (MMD) of 14 μm with only 4% of the particles being less than 4 μm in diameter. The mean concentration of sulfuric acid in the air of this other forming department was 2.7 mg/cu m. These data on particle size were cited by Williams [28] apparently as having some bearing by analogy to the conditions present in his own study. As an additional factor to particle size, the high solubility of sulfuric acid would suggest rapid absorption in the upper respiratory air passages with little effect being expected on the lower portions of the respiratory tract. In the absence of comparative data such as ambient relative humidity, temperature, and air movement, the comparisons may be uncertain.

In Egypt, El-Sadik and his associates [31] in 1972 reported on 33 workers and 20 controls "never exposed to any chemicals," in the manufacturing departments of two storage battery plants. All subjects were clinically examined, had a history taken with particular attention to respiratory symptoms, and were tested for pulmonary function (FVC and FEV 1), salivary pH, and dental anomalies. Air samples indicated

concentrations of 26 to 35 mg/cu m of sulfuric acid in one plant and 12.6 to 13.5 mg/cu m in the other. No significant difference was found in the prevalence of chronic bronchitis and/or chronic asthmatic bronchitis between exposed and control workers, based on history and examination findings. A reduction in vital capacity was found at the end of the work shift compared to the beginning of the work shift, but the group mean decrease was greater in the control than in the exposed group. On the other hand, there was a greater group mean decrease in FEV 1 in the exposed group than in the controls. The authors recognized that this might be due to the inhalation of sulfuric acid mist. There was a slightly greater acidity in the salivary pH in the exposed group than in the control group during the course of the work shift. As to dental anomalies, almost 40% of the exposed workers were found to have dental erosion and more dental discoloration than the controls. Dental loss and infection rates were, however, slightly higher in the controls.

In 1961, Malcolm and Paul [20] reported on dental erosion in 160 men exposed to sulfuric acid mist in the manufacture of storage batteries. Concentrations, measured on a dry day with low relative humidity, varied from 3.0 to 16.6 mg/cu m in the forming process, and from less than 0.8 to 2.5 mg/cu m of air in the charging process. An additional 117 workers from other parts of the plant free from sulfuric acid mist were studied as controls. The prevalence and graded severity of dental erosion and decayed, missing, and filling

rates were compared in the three groups: high level sulfuric acid exposure (forming), low level exposure (charring), and unexposed controls. Etching of the dental enamel (a change in surface texture without loss of tooth substance) was found most commonly in the highest exposed group, less so in the lower exposed group, and was absent from the controls. The lowest grade of dental erosion defined, loss not exceeding 2 mm of incisal enamel, along with etching, was most prevalent in the high exposed group (55 out of 63, 87%), less so in the lower exposed group (7 out of 15, 47%), and absent in the controls. The differences were highly significant (p less than 0.01). The two higher grades of erosion, loss of 2 to 5 mm of tooth crown and loss of more than 5 mm of tooth crown, were present in the high exposed group only. Additionally, of 7 men transferred from the forming department of another factory, 6 showed advanced stages of erosion and the seventh had dentures. This small group had a mean length of exposure of 5 years, which was far less than that at the main factory. It was established that dental etching and erosion occurred only on the anterior teeth (central and lateral incisors, and to a much smaller extent, the canines) to the extent that these teeth were directly exposed to the impingement of acid droplets, as left uncovered by the lips in their customary position. Six workers from the high exposed group were unaffected by the acid. This was postulated to be due either to resistance of the enamel or to the individuals seldom parting their lips, thus preventing acid mist from reaching

the teeth. Also, it seems that time-on-the-job could have been a factor; the employment duration was not given for these workers.

In a comprehensive study of the problem of dental erosion in all those industries which involve exposure to any significant concentration of acid spray or mist, ten Bruggen Cate [19] in 1968 reported on 555 "acid workers" over a two-year observation period in Britain. The study was initiated in response to a memorandum [32] to the Industrial Injuries Advisory Council from the British Dental Association which concluded that industrial dental erosion was a hazard which existed, and that in the majority of cases severe dental damage resulting in disfigurement occurred. Of the total workers studied, 101 workers were exposed essentially to sulfuric acid alone, the other workers being exposed primarily to hydrochloric, nitric, hydrofluoric, chromic, and phosphoric acids in a wide variety of industries (48 firms) and processes. All control workers came from acid-free departments of the firms participating in the survey and all controls were found to be free from industrial dental erosion. All 555 workers studied had natural teeth, 38% having been excluded because their teeth had been extracted and descriptions of the conditions of their teeth prior to removal were unreliable. The classification of dental erosion used previously by Malcolm and Paul [20] proved unsatisfactory because it was necessary to subtract the remaining tooth substance from assumed dimensions of the original crown in order to estimate tooth loss. A

classification was therefore selected ranging from etching, loss of enamel only (Grade 1), loss of enamel with involvement of dentine (Grade 2), further exposure of secondary dentine (Grade 3), to loss resulting in pulpal exposure (Grade 4). Interestingly, no Grade 4 erosion was observed. It was suggested that pain would lead to early treatment of such an erosion, in most cases resulting in extraction. Further, pain was very rarely reported, and when present, was described as a hypersensitivity to cold. Only 5 cases reported pain for which erosion was considered to be the cause. In the storage battery industry involving almost exclusively exposure to sulfuric acid mist, nearly 20% of the forming workers showed Grade 2 or Grade 3 erosion at the first examination. Erosion was less in the charging departments, yet some of these workers had been employed for only short periods and showed progressive erosion at subsequent examinations. Erosion was also present in other acid-using industries, although the prevalence was consistently less than that observed among battery, particularly formation, workers.

A relationship was observed between the onset and advance of erosion and the length of service. Grade 1 erosion occurred in 4 to 6 months, Grade 2 erosion in 2 to 5 years, and the earliest Grade 3 cases, in 6 to 10 years. Results showing progressive erosion indicated that the battery formation process was the most likely to produce dental erosion, based on cases actually observed to advance under modern (1964) industrial environmental conditions. It was emphasized

that erosion could be greatly reduced or even eliminated by installation of effective control measures, such as efficient exhaust systems.

Functional disability and disfigurement occurred although little evidence was seen of treatment to restore function or appearance to acid-eroded natural teeth. This was believed due to the fact that many workers were not interested in the level of dental treatment required or were not aware that treatment was possible. Additionally, it was concluded that acid environments had no influence on the incidence of caries.

Animal Toxicity

Treon et al [33] in 1950 reported a comparative mortality study in guinea pigs, rabbits, rats, and mice exposed to high concentrations of sulfuric acid aerosol (87 to 1,600 mg/cu m) in which about 95% of the particles were below 2 μ m in diameter. Guinea pigs succumbed after having been exposed for a brief period to 87 mg/cu m. Animals of other species survived after being exposed at this concentration for 2.75 hours, and much higher concentrations were required to produce death. Some mice died following exposure to 549 mg/cu m for 3.5 hours, exposure to 699 mg/cu m was lethal to rats, while higher concentrations were required to cause death in rabbits. Deaths occurred almost uniformly when groups of mice, rabbits, and rats were exposed to a concentration of 383 mg/cu m for 7 hours on each of five successive days. All mice, rats, and rabbits, however, survived

exposure for the same duration to 203 mg/cu m. Therefore, the order of increasing sensitivity established was rabbits, rats, mice, and guinea pigs. Concentration rather than duration was more critical in the mortality of guinea pigs. Lesions produced included degenerative changes in the epithelium of the respiratory tract, pulmonary hyperemia and edema, and focal pulmonary hemorrhages. The lungs of all animals exposed showed areas of atelectasis and emphysema.

Amdur et al [34] found the 8-hour LC50 (concentration lethal to 50% of the animals) of sulfuric acid aerosol of mass median diameter (MMD) of 1 μ m to be 18 mg/cu m for 1- to 2-month old guinea pigs and 50 mg/cu m for 18-month old animals. The cause of death in the animals dying within 2 hours appeared to be asphyxia caused by bronchoconstriction and laryngeal spasm. Animals dying after longer exposures showed gross capillary engorgement and hemorrhage. When the exposure times were extended to 72 hours, there was no mortality at 8 mg/cu m; thickening of alveolar walls and areas of consolidation were found. Longer exposures at higher concentrations did not increase mortality beyond that observed at 8 hours at a given concentration, but the above-mentioned lung changes were much more marked. It was postulated that the toxicity of sulfuric acid aerosol for the guinea pig has two aspects: it promotes laryngeal spasm and bronchospasm which may be lethal depending on the concentration and, in addition, it causes parenchymal lung damage, dependent upon the total dose represented by the product of concentration and time.

Thomas et al [35] reported exposing guinea pigs for longer periods (18 to 140 days) to mean concentrations mostly from 1 to 4 mg/cu m and with 3 different particle sizes, 0.6, 0.9, and 4 μ m. Of the 3 particle sizes used, 0.9 μ m produced the greatest effects including slight lung edema and rare capillary hemorrhages. There was some increase in desquamated epithelial cells in the minor bronchi. Slight edema of the larynx and trachea and a decrease in mucus in the major bronchi were seen with the 4- μ m particles. It was concluded that the guinea pig can tolerate levels of 2 mg/cu m for more than 3 months of continuous exposure with only minor pathological effects.

Bushtueva [36] reported exposing guinea pigs to 2 mg/cu m sulfuric acid aerosol of unspecified particle size for 5 days and found edema and thickening of the alveolar walls. One- to 2-weeks following exposures to 2 mg/cu m, a slight catarrhal reaction in the tracheal and bronchial mucosa with interstitial proliferative processes was observed accompanied by round lymphoid cell infiltration around blood vessels and bronchi. These changes seemed to progress with prolonged exposure up to 2 and 3 months.

Amdur [37] studied the effects on airway resistance in guinea pigs of sulfuric acid aerosol of 0.8-, 2.5-, and 7- μ m MMD in concentrations ranging from 2 to 40 mg/cu m. The largest particles, 7 μ m, even at a concentration as high as 30 mg/cu m, caused only a slight increase in airway resistance. Such particles would probably not penetrate beyond the nasal passages. The 0.8- μ m particles produced a significant increase in resistance, even at 1.9 mg/cu m concentration. At 40 mg/cu m,

the 2.5- μ m particles produced the greatest increase in resistance, but at concentrations below 2.0 mg/cu m, the 0.8- μ m particles produced the greater effect. In general, it was concluded that large particles which reached the middle respiratory tract (trachea and bronchi) probably acted by producing mucosal swelling, secretion, and exudation of fluid which lead to obstruction of major airways, whereas the smaller particles produced simple reflex bronchoconstriction. [37]

Lewis et al [38] studied the effects of sulfuric acid mist, alone (0.755 mg/cu m) and in combination with sulfur dioxide (5.1 ppm sulfur dioxide + 0.835 mg/cu m sulfuric acid) on the diffusion capacity, pulmonary compliance and resistance, and residual volumes of purebred beagles. The duration of exposures was 21 hours daily for 225 days. Half the dogs had previously been "impaired" by exposure to 26 ppm nitrogen dioxide for 191 days. The main observed effect of sulfuric acid exposure in these experiments was a statistically significant reduction in mean diffusion capacity (measured by the single-breath carbon monoxide method) which was independent of the effect of previous nitrogen dioxide impairment or concomitant exposure to sulfur dioxide. Dogs that were exposed to sulfur dioxide and sulfuric acid without previous impairment by nitrogen dioxide had a smaller "residual volume" than any other experimental group.

In a later report, Lewis et al [39] studied the effects in beagles of exposure to 0.9 mg/cu m sulfuric acid alone and in combination with 13.4 mg/cu m sulfur dioxide on certain hematological

indices, organ weights at autopsy, and lung function indices similar to those studied earlier. [38] Exposure to sulfuric acid, with or without concomitant sulfur dioxide, for 225 or 620 days had no demonstrable effect on the white cell count or on erythropoiesis. Statistically significant decreases in both lung and heart weights in the dogs exposed to sulfuric acid aerosol were observed as compared with total body weight. It was hypothesized that this might either be an effect of elevated blood sulfate bathing those organs, or a neural or humoral response to injury to the lung. The effect of sulfuric acid exposure on lung function, as in the earlier series of experiments, was most marked in decreasing diffusion capacity. In the opinion of the authors their findings indicated that continuous chronic inhalation of 0.9 mg/cu m sulfuric acid mist had a deleterious effect, in beagles, on both the conducting airways and the lung parenchyma.

In 1954, Amdur [25] reported the effects of a combination of sulfuric acid mist at 8 mg/cu m and sulfur dioxide at 89 ppm on growth, lung pathology, and respiratory response. In 8 guinea pigs exposed for 8 hours, weight had decreased the day following exposure and growth was slower to resume than was observed for either agent administered separately. Two guinea pigs were exposed 72 hours following the initial exposure to the same concentrations for another 8 hours. In these reexposed animals, growth ceased entirely during the period of observation following reexposure. Pathologic lung changes

were also more extensive than that observed for either agent alone, consisting of large areas of complete consolidation and hepatization involving entire lobes in all cases. In the reexposed animals, extensive hemorrhage and consolidation were present. It was commented that the general ill health of the animals was very likely related to the presence of the extensive lung damage. Labored breathing was very pronounced, continuing for 24 to 48 hours after exposure. In contrast, there were no noticeable respiratory effects in guinea pigs exposed to 8 mg/cu m sulfuric acid mist alone. Restlessness and annoyance initially appeared in animals exposed to 89 ppm sulfur dioxide alone, but that disappeared after approximately 5- to 10-minutes exposure. It was therefore concluded that the effects on growth, lung changes, and respiration were much more marked than would have been predicted from the use of either agent alone.

Correlation of Exposure and Effect

Because of the widespread use of sulfuric acid in industry, reports appear frequently of accidental skin or eye contact with the acid. The vast majority of cases where exposures through surface contact with the acid occur, either from splash or spray, can be attributed to some type of equipment malfunction. Because of the sudden and frequently unanticipated occurrences of acute occupational exposures, concentrations are difficult to establish. The case report presented by Goldman and Hill [14] emphasizes the severe damage caused to a worker when sprayed in the face with liquid

oleum resulting from a burst valve. Even with use of a safety shower, exposure was sufficient to cause second and third degree burns of the face and body and pulmonary edema due to sulfuric acid inhalation. Chronic after-effects were manifested as pulmonary fibrosis, residual bronchitis, and pulmonary emphysema. In addition, burning and charring of the skin were sufficient to cause marked scarring and disfigurement.

The epidemiologic studies concerning the health effects resulting from sulfuric acid exposure are difficult to correlate with environmental concentrations, either because environmental sampling was not performed, because data were unavailable for inclusion in the studies, or because sampling and analytical procedures made environmental results very questionable (see Environmental Data). The 1970 study by Williams [28] for lead-acid battery workers indicated that forming process workers and ex-workers had more spells of sickness absence due to respiratory disease than was expected from a calculated absence rate for all men. Pasting and assembly workers (controls) had fewer spells than expected. Statistically significant decreases were noted in mean forced vital capacity (FVC) and forced expiratory volume at one second (FEV 1), but the differences were attributed to possibly circadian (presumably day-night) variation. However, the FVC and FEV 1 decreases were somewhat larger in the exposed than in the control groups. No environmental measurements were made expressly for this study [28]; however, estimates from other studies conducted in the same plant indicated environmental sulfuric acid levels to vary from 3 to 16.6 mg/cu m, taken on a single day and reported in the dental erosion

study by Malcolm and Paul. [20] The second estimate, 1.4 mg/cu m (range, 0.2 to 5.6 mg/cu m), was reported by Anfield and Warner [29] 6 years after the end of Williams' [28] sickness absence study. Williams [28] concluded that an excess of spells of respiratory disease, especially bronchitis, occurred in the forming group workers manufacturing the lead-acid batteries.

El-Sadik et al [31] reported environmental concentrations of 25 to 35 mg/cu m of sulfuric acid in one storage battery plant and 12.6 to 13.5 mg/cu m in another (see Environmental Data). No significant difference was found in the incidence of chronic bronchitis or chronic asthmatic bronchitis between 33 exposed workers and 20 controls. Changes in vital capacity and FEV 1 were similar to those observed by Williams [28] and there was a greater group mean decrease in FEV 1 in the exposed group than in the controls. The authors [31] suggested that the decreased FEV 1 might be due to the inhalation of sulfuric acid mist. In addition, the sulfuric acid exposed workers showed a nearly 40% higher occurrence of dental erosion and dental discoloration than was noted in the controls.

The studies on dental erosion reported by Malcolm and Paul [20] in 1961 and by ten Bruggen Cate [19] in 1968 demonstrated a high incidence of dental damage among forming process workers and among charging workers, with dental erosion being absent in all of the controls (p less than 0.01). [20] Airborne acid concentrations varied from 3.0 to 16.6 mg/cu m in the forming process and from less than 0.8 to 2.5 mg/cu m in the charging process. [20] A positive relationship was also observed [19] between the

onset and advance of dental erosion and the length of service. In addition, functional disability and disfigurement occurred, although there appeared to be no influence of acid environments on the incidence of dental caries. [19]

Human experimental exposure studies have included changes in respiratory airway resistance [27] and changes studied by measurement of sensory and central nervous system responses from light sensitivity in the dark adapted eye or from reflex optical stimulation. [18] In addition, determinations have been made on the lower limits of detection of sulfuric acid. [12, 16, 18] Bushtueva [18] reported erratic changes in respiratory amplitude and an increase in respiratory rate at sulfuric acid concentrations of 1.8 to 2 mg/cu m. Very slight changes were noted at 1.0 to 1.1 mg/cu m and no effects were obtained at concentrations below 1 mg/cu m. Amdur et al [16] reported an increased respiratory rate in all subjects tested at 0.35, 0.40, and 0.50 mg/cu m. At 1.0 mg/cu m, forced expiration was noted and at 2 mg/cu m the increased rate was more rapid and marked. Effects were even more marked and varied at 5 mg/cu m. Morando [26] reported similar results at 0.52 to 0.7 mg/cu m. Bushtueva [24] reported prolongation of optical chronaxy at 0.73 mg/cu m sulfuric acid (0.6 mg/cu m was subthreshold) and an increase in sensitivity to light during dark adaptation at 0.7 mg/cu m (0.3 mg/cu m was subthreshold). The subjective limit of detection to sulfuric acid has been reported to be between about 0.5 and 0.7 mg/cu m by a number of investigators. [12, 16, 18]

Sulfuric acid exposures are lethal to mice, rabbits, and rats at about 400 mg/cu m of air for exposure periods of 7 hours a day for 5

days. [33] Guinea pigs are much more susceptible, however, 87 mg/cu m being lethal after only brief exposure periods accompanied by degenerative changes of the respiratory epithelium, pulmonary edema, and hemorrhages. The lungs of all animals exposed showed areas of atelectasis and emphysema. [33] Amdur et al [34] reported the 8-hour LC50 to be 18 mg/cu m for young guinea pigs (1 to 2 months old) and 50 mg/cu m for 18 month old animals. Sulfuric acid exposures of 8 mg/cu m for 72 hours produced no mortality. Further, no changes in respiratory effects were noted in guinea pigs exposed at 8 mg/cu m sulfuric acid. [25] At exposure levels of 2 mg/cu m, Thomas et al [35] reported minor pathological changes in guinea pigs after more than 3 months and Bushtueva [36] reported edema and thickening of alveolar walls after 5 days' exposure. Lewis et al [39] considered that the continuous chronic inhalation (225 days) of 0.9 mg/cu m sulfuric acid had a deleterious effect on beagles on both the conducting airways and the lung parenchyma.

Particle (droplet) size seems to interplay along with temperature and humidity to influence the toxic effects of sulfuric acid in the respiratory tract. Amdur [37] found that 2.5 μm particles produced a marked increase in pulmonary flow resistance at a concentration of 40 mg/cu m. However, median particle sizes of about 0.8 μm were more effective at concentrations below 2.0 mg/cu m. It was concluded that large particles probably exerted their effects on the middle respiratory tract (trachea and bronchi) whereas the smaller particles produced simple reflex bronchoconstriction. [37] Thomas et al [35] found

similar results in guinea pigs with particle sizes of 0.6, 0.9, and 4 μm . The animal mortality studies of Treon et al [33] and Amdur et al [34] were performed with median particle sizes of sulfuric acid mist less than 2 μm . In contrast, the human experimental study of Toyama and Nakamura [27] reported a greater mean increase in pulmonary airway resistance (36.5%) in subjects exposed to 0.8 to 1.4 mg/cu m sulfuric acid of 4.6 μm particle size. A 17.9% increase in airway resistance was found for a reported sulfuric acid concentration of from 0.01 to 0.1 mg/cu m of air at 1.8 μm particle size. These results are difficult to evaluate because of the method by which the sulfuric acid was generated. An interactive effect was indicated between hydrogen peroxide and sulfur dioxide rather than to sulfuric acid alone. A comment given by Williams [28] in his epidemiologic study may be pertinent at this point to reflect particle sizes in an occupational situation. Although mist particle size was not measured in the Williams study, a forming process department of another similar factory was reported to demonstrate acid mist having a mass median diameter of 14 μm with only 4% of the particles being less than 4 μm in diameter.

The interaction of sulfuric acid with other gases and aerosols has been reported. Amdur [25] reported that a combination of sulfuric acid mist at 8 mg/cu m in guinea pigs (which produced no noticeable respiratory effects when administered alone) and 89 ppm sulfur dioxide produced effects on growth, lung changes, and respiration which were more marked than would have been predicted from the use of either agent

alone. Bushtueva, [24] however, reported that in humans 0.7 mg/cu m sulfuric acid (which was a threshold concentration) and 3 mg/cu m sulfur dioxide produced simple physiological summation of effects as measured by light sensitization to the dark adapted eye. Similar additive effects were noted for optical chronaxy at 0.73 mg/cu m sulfuric acid and 1.5 mg/cu m sulfur dioxide. Lewis et al [38] reported a statistically significant reduction in mean diffusion capacity in beagles exposed 21 hours a day for 225 days to a combination of 0.835 mg/cu m sulfuric acid and 5.1 ppm sulfur dioxide. The reduction was greater than that which would have been expected by either agent alone. Further studies by Lewis et al [39] showed statistically significant decreases in both lung and heart weights as compared with total body weight to exposures at 0.9 mg/cu m sulfuric acid and 13.4 mg/cu m sulfur dioxide. The human study on sulfuric acid exposure reported by Toyama and Nakamura [27] appears to resemble more closely a combination study between hydrogen peroxide and sulfur dioxide rather than sulfuric acid because of the manner in which the substances were administered.

Humidity also seems to play a role in influencing the effects of sulfuric acid exposure. Sim and Pattle [17] reported a greater increase in pulmonary airway resistance in humans exposed to 20.8 mg/cu m sulfuric acid at 91% humidity as compared with 39.4 mg/cu m at 62% relative humidity. The lower dose under conditions of high humidity was also more irritating to the respiratory tract than the higher dose under the less humid conditions.

IV. ENVIRONMENTAL DATA

Environmental Concentrations

Data on occupational environmental concentrations of sulfuric acid are very meager, possibly because the corrosive action of the acid on the skin and eyes is so commonly recognized from splash and spray that environmental levels have been overlooked. The few data that are available have generally been collected only on a single day; therefore, it is extremely difficult to relate the reported environmental information to actual conditions. At best, only rough estimates of environmental concentrations, especially ranges, can be made. Occupational environmental levels reported by Malcolm and Paul, [20] El-Sadik et al, [31] and Anfield and Warner [29] are as meaningful as could be obtained.

Malcolm and Paul's study [20] concerned dental erosion in workers. Reported acid mist concentrations in forming process areas to a mixture of dilute sulfuric acid (specific gravity 1.020 to 1.100) varied from 3.0 to 16.6 mg/cu m of air. Measurements were made on a dry day with low relative humidity. Forming tanks contained a foaming agent on the top of the acid which coalesced acid-containing gas bubbles, thus reducing acid mist escaping into the air. In addition, impervious sheets were used to cover the tanks which condensed the spray and permitted it to run back into the tanks. It was stated that the amount of acid present in the air on a cold humid day often exceeded 16 mg/cu m. In the charging process, the acid specific gravities were mostly about 1.265, higher than those in

the forming process, and airborne acid levels varied from less than 0.8 to 2.5 mg/cu m. The method of analysis was not given; however, the standard error of the method was reported to be $\pm 25\%$. These same environmental data were the only ones referred to in the epidemiologic study on dental erosion reported by ten Bruggen Cate [19] in 1968.

El-Sadik et al [31] reported environmental sulfuric acid concentrations, again in the manufacture of storage batteries. Concentrations ranged from 26.12 to 35.02 mg/cu m of air in 1 plant and 12.55 to 13.51 mg/cu m in another. No information was given as to what processes or what locations were involved, nor was temperature, humidity, particle size, etc. mentioned. Air samples were collected at 2 liters/minute in a bubbler containing sodium hydroxide absorbing solution and methyl red indicator. Twelve samples were collected daily at various times (unspecified) and analyzed for excess sodium hydroxide by standard acid titration. The method employed was a common acid-base titration and was not specific for sulfuric acid; however, acid exposures in battery manufacturing processes are almost exclusively due to sulfuric acid mist.

Anfield and Warner, [29] in response to the limited information available for sulfuric acid mist concentrations in industrial atmospheres, reported on environmental monitoring of sulfuric acid, sulfur dioxide, and ferrous sulfate in 5 industrial operations. The departments reported were Department A, a continuous sheet strip acid cleaning (pickling) operation of a large integrated steel plant; Department B, an acid

recovery plant at the same steel facility; Department C, an acid cleaning (pickling) operation which treated small steel components for the automobile industry; and Departments D and E, lead-acid battery plate forming operations at 2 separate plants. A sampling train consisting of a filter head with filter, an impinger containing hydrogen peroxide absorbing solution, a gas meter, and a vacuum pump was used for sample collection. The air was sampled approximately 5 feet above floor level for periods varying from 1/2 hour up to several hours at flow rates up to 20 liters/minute. Because the sulfuric acid and particulate sulfate collected on the filter could not be determined separately, 2 samples were taken so that each substance could be analyzed separately. The sulfur dioxide passed through the filter and was absorbed in the hydrogen peroxide solution. The results of the sulfuric acid determinations are listed in Table X-4. Considerable ranges in acid levels occurred, reportedly due to different processes in various parts of the departments, changes in rates of production, and the effects of natural and forced ventilation systems. The importance of enclosure, ventilation, or a combination of these practices was emphasized. Department C, from a series of 85 samples around an open, unventilated tank, showed average sulfuric acid concentrations of approximately 3 mg/cu m. The 6 highest samples averaged more than 14 mg/cu m, and 49 samples exceeded 1 mg/cu m. The 15 lowest samples averaged 0.36 mg/cu m. Department A, also employing a pickling process, but utilizing enclosure and exhaust ventilation, showed only 2 of 48 samples which exceeded 1 mg/cu m, and the overall average concentration was 0.33 mg/cu m. The plate-forming operations at the 2

battery manufacturing plants, Departments D and E, showed average concentrations of 1.38 and 0.97 mg/cu m, respectively. In both installations, the operations were partly enclosed or a detergent was used to provide a frothing seal.

In a simple laboratory experiment conducted in an exhaust hood with a beaker of 15% w/v sulfuric acid solution and a filter sampler located "a few inches" above the beaker, Anfield and Warner [29] demonstrated that although heating and agitation of fluid with an air bubbler would increase airborne sulfuric acid concentrations, processes involving the evolution of hydrogen produced enormously high acid levels by comparison. Heating alone produced concentrations of 0.045 mg/cu m at 90 C, 4.1 mg/cu m with agitation at the same temperature, but with hydrogen bubble evolution, concentrations of 3.2 mg/cu m were noted at 20 C, 278.9 mg/cu m at 60 C, and complete collapse of the filter resulted at 90 C. The additional use of floating plastic balls to blanket the reaction in the 60 C range reduced sulfuric acid mist emanation by 50% (from 278.9 to 136.0 mg/cu m).

If exhaust ventilation is necessary for control of sulfuric acid mist, design principles which give useful guidelines are published for general industrial ventilation practices, [40] open-surface tanks, [41] and design and operation of local exhaust systems. [42]

Environmental Sampling and Analytical Method

Early collection methods for sulfuric acid in air involved the use of water or alkaline solutions in a scrubber or impinger followed by some form of acid-based titration. [1,43] Such methods also absorbed sulfate salts and possibly acid gases. Sulfate measurements using filtration or impaction techniques have been used in air pollution studies by titration for total acidity [13,44] or by a related procedure of sulfate analysis through the use of a barium sulfate turbidimetric determination. [45] The use of selective filters to separate sulfuric acid (with sulfates) from sulfur dioxide has also been reported. [46,47]

In 1969, Scaringelli and Rehme [47] reported a method for measuring sulfuric acid aerosol in microgram quantities which had application for community air measurements. The method successfully separated sulfuric acid from sulfur dioxide and other sulfates by filter collection with controlled temperature (400 C) in a nitrogen atmosphere, followed by conversion to sulfur dioxide with hot copper which could then be determined by spectrophotometric, coulometric, or flame photometric techniques. The method, although satisfactory for sulfuric acid isolation, required controlled heat, a rather special setup of apparatus, and a zirconium oxide combustion tube, thus entailing a rather complicated preparation procedure prior to the analytical determination. Dubois et al [48] devised a microseparation of sulfuric acid from other airborne sulfates by the microdiffusion of sulfuric acid at 200 C into sodium hydroxide absorbing solution using glass petri dishes. Subsequently, following the preliminary

separation, the isolated sulfuric acid was then measured by a method specific for sulfate. [49]

Because gravimetric determinations with sulfate were both time-consuming and tedious, and turbidimetric procedures were often unreliable and difficult to reproduce, direct titration methods for sulfate were devised which were rapid, accurate, and widely applicable. [49,50] Fritz and Freeland [50] in 1954 described the direct titration of sulfate in an alcoholic solution with barium chloride or barium perchlorate using Alizarin Red S or Thorin [o-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid] as the indicator. A sharp, vivid color change from yellow to pink was described as marking the endpoint with results being as precise as gravimetric procedures and considerably faster. Later Fritz and Yamamura [49] in 1955 improved the method so as to be capable of determining very low concentrations of sulfate, as low as 10 ppm in water samples. The barium perchlorate titration method has been capable of measuring sulfuric acid concentrations at 0.1 mg/cu m (see Appendix I) and results from a micromethod have been reported in the range of 1 microgram/cu m of air. [48]

The filtration method accompanied by direct titration with barium perchlorate using Thorin as the indicator is the recommended compliance method as outlined in Appendix I. Metal ion interferences are eliminated by use of an ion exchange column and phosphate can be removed by precipitation with magnesium carbonate. If circumstances are such that airborne sulfate occurs, it can be separated [48] from sulfuric acid prior to the titration with barium perchlorate.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Cook, [51] in his comprehensive 1945 list of maximum allowable concentrations (MAC) of industrial atmospheric pollutants, cited 2 different values for sulfuric acid mist, 5 mg/cu m recommended by the Industrial Hygiene Division of the New York State Department of Labor and 2 mg/cu m recommended by the Industrial Hygiene Division of the Utah Department of Health. The documentation cited by Cook included references from Flury and Zernik's "Schadliche Gase,"[52] and one from Sterner [53] endorsing the 5 mg/cu m MAC. Cook also observed that individual human susceptibility differed widely, with the development of tolerance in workers habitually exposed.

In 1952, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted 1.0 mg/cu m as their recommended Threshold Limit Value (TLV) for sulfuric acid mist. [54] This decision was based upon human experimental work reported by Amdur et al [16] in which it was found that concentrations below 1 mg/cu m could not be detected by odor, taste, or irritation by unacclimated persons. The threshold for odor and irritation was 1 mg/cu m in 2 persons and 3 mg/cu m in all subjects.

The ACGIH TLV has remained unchanged at 1.0 mg/cu m. In the latest documentation of TLV's, [55] the ACGIH Committee reviewed 8 published reports [16,20,21,23,33,34,35,37] from which the TLV of 1.0 mg/cu m was recommended to prevent irritation of respiratory passages and injury to the teeth.

In a report presented by the Czechoslovak Committee of MAC, [56] the majority of members of the Committee agreed on a MAC of 1 mg/cu m of air as a mean concentration and a peak MAC of 2 mg/cu m although it was recognized that slight irritation, though not necessarily unpleasant, might be experienced at 1 mg/cu m. The report of Amdur et al [16] was not sufficiently convincing to influence the opinion of the Committee at that time (1969). It was also commented that a great effort was necessary under the conditions of sulfuric acid production to adhere to their recommendations of 1 mg/cu m. The same standard exists in Soviet Russia, Hungary, and Poland. In the Federal Republic of Germany and the German Democratic Republic, the standard was listed as 13 mg/cu m and 10 mg/cu m, respectively.

The present federal standard for sulfuric acid is an 8-hour time-weighted average of 1 mg/cu m (29 CFR Part 1910.93 published in the Federal Register, volume 37, page 22139, dated October 18, 1972).

Basis for Recommended Environmental Standard

Although subjective responses such as throat tickling and scratching have been reported at sulfuric acid concentrations of less than 1 mg/cu m, [12,18] other investigators have reported no subjective responses until a level of 1 mg/cu m was reached. [16] Concentrations of about 5 mg/cu m may be very objectionable, usually causing cough, with marked alterations in respiration. [16] Overexposure to sulfuric acid by splash or spray has resulted in pulmonary edema and chronic pulmonary fibrosis, residual bronchiectasis, and pulmonary emphysema. [14]

Very few reports are available of occupational sulfuric acid concentrations especially reports from which exposure-effect relationships may be obtained. Environmental concentrations in the lead-acid battery industry have been reported ranging from 3 to 16.6 mg/cu m of air [20] in which relatively dilute sulfuric acid is used in forming processes. In addition, charging processes in the same industry have produced measured airborne sulfuric acid levels at about 0.8 to 2.5 mg/cu m. [20] Other studies have reported mean concentrations of 1.4 mg/cu m (range, 0.2 to 5.6 mg/cu m) [29] and findings ranging from 12.5 to as high as 35 mg/cu m. [31] These figures serve more to illustrate general circumstances for which many unknown variables exist rather than quantitative levels in attempts to derive exposure-effect relationships.

The published epidemiologic studies provide valuable information on the signs and symptoms resulting from occupational exposure to sulfuric acid. In studying sickness absence and ventilatory capacity in 461 lead-acid battery workers, Williams [28] concluded that an excess of spells of respiratory disease, especially bronchitis, occurred in forming process workers. Variation was noted in the number of spells of sickness absence which was contributed by different individuals; therefore, no tests of statistical significance were made. It was suggested that the increased number of spells of respiratory disease was due to an increased incidence of spells in attacked men rather than by an increased proportion of men attacked. It was also believed likely that one or more factors might have been present in the forming operation which was specifically associated with bronchitis and other respiratory disease. Interestingly, the same forming operation used for this study [28] was also the

source of considerable dental erosion reported by Malcolm and Paul [20] in 1961. It was suggested by Williams [28] that the absence of lower respiratory tract disease observed in his study, where marked dental erosion had been earlier reported, might have been due to the large size of sulfuric acid mist particles or droplets, thus preventing their reaching the deep lung. Williams [28] stated that other operations similar to the one being reported showed median particle sizes of 14 μ m with only 4% of the particles being less than 4 μ m in diameter. El-Sadik et al [31] found no significant difference in the prevalence of chronic bronchitis and/or chronic asthmatic bronchitis between 33 exposed workers and 20 controls; however, there was a greater group mean decrease in pulmonary function (FEV 1) in the exposed group than in the controls which the authors stated might be due to the inhalation of sulfuric acid mist. The consistent findings of dental erosion among sulfuric acid workers reported in 2 separate studies [19,20] indicates the problem to be one of definite health impairment. The consistent relationship that was observed [19] between the onset and advance of dental erosion and the length of employment emphasized this problem to be one of importance in the evaluation of sulfuric acid exposure. Progressive erosion among battery formation process workers was noted based on cases actually observed to advance under relatively modern (1964) industrial environmental conditions. Anfield and Warner [29] compared their environmental findings (see Table X-4) with those of ten Brugge Cate [19] on tooth erosion incidence and stated that their 1.4 mg/cu m finding likely underestimated the dental

risk to which workers had been exposed during their earlier years. A more realistic value of environmental acid concentration was suggested as being somewhere between 1.4 mg/cu m and that reported by Malcolm and Paul, 3 to 16.6 mg/cu m. [20] Even though dental erosion produced functional disability and disfigurement, [19] workers were able to compensate by using the canine teeth in place of the anterior teeth which could not be brought together. Because of the many uncertainties present in the reported environmental sulfuric acid levels, it is not possible to estimate an exposure level to sulfuric acid mist which would eliminate the occurrence of dental etching and erosion.

Experimental studies have shown that sulfuric acid produces mucous membrane irritation and reflex bronchoconstriction with increased airway resistance. Most animal experimental work has been conducted in guinea pigs, considered to be the most sensitive of the standard laboratory animals to the respiratory effects of sulfuric acid. [33] At concentrations considered important for the evaluation of environmental standards, exposure of guinea pigs to 2 mg/cu m sulfuric acid for 1 hour produced increases in pulmonary airway resistance from reflex bronchoconstriction. [37] Bushtueva [36] found edema and thickening of the alveolar walls of guinea pigs also exposed to 2 mg/cu m, but for 5 days continuous exposure. Thomas et al [35] reported minor unspecified pathological changes for continuous exposure periods greater than 3 months. Similarly, continuous exposure of dogs to 0.9 mg/cu m sulfuric acid for 225 days produced decreased lung function as measured by diffusion capacity and changes in lung parenchyma. [39] However, effects

produced by continuous exposure are difficult to evaluate in terms of intermittent exposures which are more representative of the occupational experience. In humans, Bushtueva [18] noted respiratory changes in amplitude and rhythm at sulfuric acid exposures of 1.8 to 2 mg/cu m. Slight changes at 1.0 to 1.1 mg/cu m, and no alterations in respiratory patterns, were noted at concentrations less than 1 mg/cu m. In another study, [24] measurements of sensory and central nervous responses from light sensitivity in the dark adapted eye or from reflex optical stimulation produced effects at 0.7 mg/cu m sulfuric acid. Both of these studies [18,24] are regarded as screening observations because results were observed in only 2 subjects. Furthermore, whether such optical changes, or for that matter, minimal respiratory changes represent undesirable effects is debatable. The increased respiratory effects reported by Amdur [16] to occur in subjects exposed to sulfuric acid concentrations as low as 0.35 mg/cu m are again uncertain as to their meaning. The findings were reported many years ago and have not been recently confirmed at the levels reported. In humans, a strong cortical influence exists to regulate respiration, and mechanical procedures, especially the use of a face mask, could influence the results markedly. In summary, the minimal changes reported in respiratory rate and on optical response to sulfuric acid concentrations below about 2 mg/cu m, remain unconvincing and unconfirmed.

The interaction of sulfuric acid with other gases and aerosols has been reported to produce effects on growth, lung changes, and respiration which were more marked than would have been predicted from

either agent alone. [25] Bushtueva [24] found the effects of sulfuric acid combined with sulfur dioxide exposure to be merely additive as measured by reflex optical responses. In dogs, statistically significant reductions in mean diffusion capacity were also found between combinations of sulfuric acid and sulfur dioxide. [39] Although Toyama and Nakamura [27] reported increases in mean pulmonary airway resistance in humans to very low concentrations of sulfuric acid (0.01 to 0.1 mg/cu m), their method of producing sulfuric acid from the reaction between hydrogen peroxide and sulfur dioxide indicated a combination effect between the 2 substances rather than to sulfuric acid alone. Although sulfuric acid was identified, no data were given concerning the amount of unreacted sulfur dioxide or hydrogen peroxide which was present with the sulfuric acid. Other investigations of particle (droplet) size, [33,34,35,37] as well as temperature effects [29] and humidity, [17] emphasize a strong interplay between these factors, thus making interpretations of exposure-effect extremely difficult. The problems encountered in interpreting results from a combination of only 2 substances emphasizes the difficulty encountered when considering particle size, temperature, humidity, and multiple substance interrelationships.

It is concluded that the existing federal standard of 1 ppm TWA should be retained. It is believed that adherence to the present environmental federal standard in conjunction with a strong program of work practices to prevent skin and eye contact from sulfuric acid will prevent the irritant effects of sulfuric acid in workers.

VI. WORK PRACTICES

The corrosive, oxidizing, and sulfonating properties of sulfuric acid are such as to require that it be handled at all times with proper care. The work practices specified in the recommended standard are primarily for the purpose of preventing or minimizing sulfuric acid contact with the respiratory tract, skin, or eyes. These practices incorporate basic principles described in standard guides such as the Chemical Safety Data Sheet SD-20, [3] and the Chemical Hazards Bulletin on Sulfuric Acid. [8]

Sulfuric acid itself is not flammable; however, it can cause ignition when in contact with other combustible materials. It reacts with some metals to release hydrogen gas, which is potentially explosive. As the gas is released from the liquid surface, it may also entrain acid droplets which may be inhaled or burn the skin. Released hydrogen will also react with arsenic, selenium, or cyanides which may be present as impurities either in the acid or in metals, producing highly toxic arsine, hydrogen selenide, or hydrogen cyanide.

Sulfuric acid generates heat when mixed with water. Adding water to the acid can be extremely dangerous; therefore, when mixing is necessary, the acid should be added to the water; in special cases when water must be added to acid, suitable precautions should be taken.

Workers should not expose themselves unnecessarily to sulfuric acid mist or fumes. Because of its irritant properties, an individual is usually conscious of the presence of acid mist in the environment, especially when the acid occurs at high concentrations. Should a situation arise where it is essential to remain in an environment where high airborne

acid levels exist, such as for repairs or in an emergency, the individual should be especially aware of the need for proper protective equipment. This should include impervious clothing, gloves, rubber shoes, goggles, face shields, and respiratory devices as appropriate to prevent acid contact with the skin, eyes, or respiratory tract.

Should an emergency make it necessary to enter a tank or closed space, reliance should never be placed on a canister-type gas mask. Only self-contained breathing apparatus in pressure-demand mode or a combination supplied air respirator, pressure-demand type, with auxiliary self-contained air supply should be used in such situations.

Employees should be trained at appropriate regular intervals in the proper techniques for handling, moving, and emptying carboys, drums, tank trucks, railroad cars, and barges of sulfuric acid. They should also be trained in the emergency procedures to be followed in case of accidents involving sulfuric acid.

All of the prescribed practices apply to oleum, which is a more hazardous form of sulfuric acid.

VII. REFERENCES

1. Jacobs MB: The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents, ed 2. New York, Interscience Publishers, 1949, vol 1, pp 311-13
2. Lewis TR, Amdur MO, Frizhand MD, Campbell KI: Toxicology of Atmospheric Sulfur Dioxide Decay Products, publication No AP-111. Research Triangle Park, NC, Environmental Protection Agency, 1972
3. Manufacturing Chemists Association: Chemical Safety Data Sheet SD-20, Rev ed--Properties and Essential Information for Safe Handling and Use of Sulfuric Acid. Washington, DC, Manufacturing Chemists Assoc, 1963, 26 pp
4. Harper HA: Review of Physiological Chemistry, ed 12. Los Altos, Calif, Lange Medical Publications, 1969, p 216
5. Fasullo OT: Sulfuric Acid, Use and Handling. New York, McGraw-Hill Book Co, 1965
6. Gafafer WM (ed): Occupational Diseases--A Guide to Their Recognition, publication No. 1097. US Department of Health, Education, and Welfare, 1964, pp 217-18
7. Statistical Abstract of the United States 1971, ed 92. US Bureau of the Census, 1971, p 708
8. American Insurance Association: Chemical Hazards Bulletin: Sulfuric Acid. C-12, Materials. March, 1966
9. Aleksieva Z: Sulphuric acid (H₂SO₄), in Encyclopedia of Occupational Health and Safety. Geneva, International Labour Office, 1972, vol 2, pp 1371-73
10. Schwartz L, Tulipan L, Birmingham DJ: A Textbook of Occupational Diseases of the Skin, ed 3. Philadelphia, Lea & Febiger, 1948, pp 234-44
11. Greenwald I: Effects of inhalation of low concentrations of sulfur dioxide upon man and other mammals. Arch Ind Hyg Occup Med 10:455-75, 1954
12. Dorsch R: [On Air Pollution by Sulfuric Acid in Battery Storage Areas and Their Surroundings.] Presented at the K. Bayer Medical School, Julius-Maximilians University, Wurzburg. Munich, G. J. Manz, 1913 (Ger)

13. Commins BT: Determination of particulate acid in town air. *Analyst* 88:364-67, 1963
14. Goldman A, Hill WT: Chronic bronchopulmonary disease due to inhalation of sulfuric acid fumes. *Arch Ind Hyg Occup Med* 8:205-11, 1953
15. Amdur MO: Aerosols formed by oxidation of sulfur dioxide. *Arch Environ Health* 23:459-68, 1971
16. Amdur MO, Silverman L, Drinker P: Inhalation of sulfuric acid mist by human subjects. *Arch Ind Hyg Occup Med* 6:305-13, 1952
17. Sim VM, Pattle RE: Effect of possible smog irritants on human subjects. *JAMA* 165:1908-13, 1957
18. Bushtueva KA: The determination of the limit of allowable concentration of sulfuric acid in atmospheric air, in *Limits of Allowable Concentrations of Atmospheric Pollutants*, Bk 3. BS Levine (transl), US Dept of Commerce, 1957, pp 20-36
19. ten Bruggen Cate HJ: Dental erosion in industry. *Br J Ind Med* 25:249-66, 1968
20. Malcolm D, Paul E: Erosion of the teeth due to sulphuric acid in the battery industry. *Br J Ind Med* 18:63-69, 1961
21. Pelnar T: [The Influence of Work in Sulfuric Acid Production on Employee Health.] *Prac Lek* 3:287-94, 1951 (Pol)
22. Best HB, Taylor NB: *The Physiological Basis of Medical Practice*, ed 8. Baltimore, Williams & Wilkins, 1966, pp 1306-07
23. Raule A: [Occupational Disease Caused by Sulfuric Acid.] *Med Lav*:590-99, 1954 (Ital)
24. Bushtueva KA: Threshold reflex effect of SO₂ and sulfuric acid aerosol simultaneously present in the air, in *Limits of Allowable Concentrations of Atmospheric Pollutants*, Bk 4. BS Levine (transl), USPHS, 1961, pp 72-79
25. Amdur MO: Effect of a combination of SO₂ and H₂SO₄ on guinea pigs. *Public Health Rep* 69:503-06, 1954

26. Morando A: [Experimental and Clinical Contribution to the Pathology of Sulfuric Acid Fumes in Man.] Med Lav 47:557-61, 1956 (Ital)
27. Toyama T, Nakamura K: Synergistic response of hydrogen peroxide aerosols and sulfur dioxide to pulmonary airway resistance. Ind Health 2:34-45, 1964
28. Williams MK: Sickness absence and ventilatory capacity of workers exposed to sulfuric acid mist. Br J Ind Med 27:61-66, 1970
29. Anfield BD, Warner CG: A study of industrial mists containing sulphuric acid. Ann Occup Hyg 11:185-94, 1968
30. Manual of the International Statistical Classification of Diseases, Injuries, and Causes of Death. Geneva, World Health Organization, 1967, vol 1
31. El-Sadik YM, Osman HA, el-Gazzar RM: Exposure to sulfuric acid in manufacture of storage batteries. J Occup Med 14:224-26, 1972
32. British Dental Association: Memorandum on the erosion of teeth, presented to the Industrial Injuries Advisory Council. Br Dent J 106:239-42, 1959
33. Treon JF, Dutra FR, Cappel J, Sigmon H, Younker W: Toxicity of sulfuric acid mist. Arch Ind Hyg Occup Med 2:716-34, 1950
34. Amdur MO, Schulz RZ, Drinker P: Toxicity of sulfuric acid mist to guinea pigs. Arch Ind Hyg Occup Med 5:318-29, 1952
35. Thomas MD, Hendricks RH, Gunn FD, Critchlow J: Prolonged exposure of guinea pigs to sulfuric acid aerosol. Arch Ind Health 17:70-80, 1958
36. Bushtueva KA: The toxicity of H₂SO₄ aerosol. Gig Sanit 22:17-22, 1957, in USSR Literature on Air Pollution and Related Occupational Diseases, A Survey, vol 1. BS Levine (transl), USPHS, 1960, pp 63-66b
37. Amdur MO: The respiratory response of guinea pigs to sulfuric acid mist. Arch Ind Health 18:407-14, 1958
38. Lewis TR, Campbell KI, Vaughan TR, Jr: Effects on canine pulmonary function via induced NO₂ impairment, particulate interaction, and subsequent SO₂. Arch Environ Health 18:596-601, 1969

39. Lewis TR, Moorman WJ, Ludmann WF, Campbell KI: Toxicity of long-term exposure to oxides of sulfur. Arch Environ Health 26: 16-21, 1973
40. Committee on Industrial Ventilation: Industrial Ventilation--A Manual of Recommended Practice, ed 12. Cincinnati, ACGIH, 1972
41. Practices for Ventilation and Operation of Open-surface Tanks, Z9.1. New York, ANSI, 1971
42. Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2. New York, ANSI, 1971
43. Patty FA: Industrial Hygiene and Toxicology, ed 2, DW Fassett, DD Irish (eds), New York, Interscience Publishers, 1962, vol II, pp 895-96
44. Mader PP, Hamming WJ, Bellin A: Determination of small amounts of sulfuric acid in the atmosphere. Anal Chem 22:1181-83, 1950
45. Roesler JF, Stevenson HJR, Nader, JS: Size distribution of sulfate aerosols in the ambient air. J Air Poll Contr Assoc 15:576-79, 1965
46. Criteria for a Recommended Standard....Occupational Exposure to Sulfur Dioxide. US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1974
47. Scaringelli FP, Rehme KA: Determination of atmospheric concentrations of sulfuric acid aerosol by spectrophotometry, coulometry, and flame photometry. Anal Chem 41:707-13, 1969
48. Dubois L, Baker CJ, Teichman T, Zdrojewski A, Monkman JL: The determination of sulphuric acid in air: a specific method. Mikrochim Acta 2:269-79, 1969
49. Fritz JS, Yamamura SS: Rapid microtitration of sulfate. Anal Chem 27:1461-64, 1955
50. Fritz JS, Freeland MO: Direct titrimetric determination of sulfate. Anal Chem 26:1593-95, 1954
51. Cook WA: Maximum allowable concentrations of industrial atmospheric contaminants. Ind Med 14:936-46, 1945

52. Flury F, Zernik F: [Noxious Gases, Vapors, Mist, Smoke and Dust Particles.] Berlin, Springer, 1931, pp 139-46 (Ger)
53. Sterner JH: Determining margins of safety--Criteria for defining a "harmful" exposure. Ind Med 12:514-18, 1943
54. Threshold limit values for 1952, adopted at the meeting of the ACGIH in Cincinnati, April, 1952. Arch Ind Hyg Occup Med 6:178-79, 1952
55. Sulfuric Acid, in Documentation of the Threshold Limit Values for Substances in Workroom Air, ed 3. Cincinnati, ACGIH, 1971, pp 239-40
56. Czechoslovak Committee of MAC: Documentation of MAC in 186 Czechoslovakia. Prague, Czechoslovak Committee on MAC, 1969, pp 148-50

VIII. APPENDIX I
METHOD FOR SAMPLING AND ANALYTICAL
PROCEDURES FOR DETERMINATION OF SULFURIC ACID

The following sampling and analytical method for analysis of sulfuric acid in air employs collection on a cellulose membrane filter, aqueous desorption, and volumetric titration in alcoholic solution. The analytical method is derived from Fritz and Freeland [50] and Fritz and Yamamura. [49]

General Requirements

Sulfuric acid concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include:

- (1) The date and time of sample collection
- (2) Sampling duration
- (3) Volumetric flowrate of sampling
- (4) A description of the sampling location
- (5) Other pertinent information

Breathing-Zone Sampling

Breathing-zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and shall

characterize the exposure from each job or specific operation in each production area.

(a) Sampling Equipment

A calibrated personal sampling pump with flowmeter (range up to 2 liters/minute), and an 0.8 μm nominal pore size cellulose membrane filter mounted into either 2- or 3-piece filter cassettes shall be used for sample collections.

(b) Sampling Procedure

The cassette containing the filter is connected to the personal sampling pump inlet by a piece of flexible vinyl tubing of convenient length, but not in excess of 3 feet. The filter assembly is attached to the worker's clothing so as to sample from the worker's breathing zone. A 100-liter sample is recommended to be collected at a rate of 1.5 liters/minute. If sulfuric acid concentrations greater than 5 times the standard are expected, smaller air volumes may be collected, but never less than 10 liters.

A minimum of 3 samples shall be taken for each operation (more samples if the concentrations are close to the standard) and averaged on a time-weighted basis. At least one blank filter with cassette shall be provided which has been subjected to the same handling as the samples but through which no air has been sampled. One additional blank filter with cassette shall be supplied with every 10 samples obtained.

Shipping

The cassette with samples are collected, along with the appropriate number of blanks, and shipped to the analytical laboratory in a suitable container to prevent damage in transit.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the pump's indication. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump received hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibrating instruments such as a wet test meter or dry gas meter can be used. The actual setup will be the same for all instruments. Instructions for

calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used.

(a) Flowmeter Calibration Test Method

The calibration setup for personal sampling pumps with the sampling system of a cassette with filter is shown in Figure X-1.

(1) Procedure

(A) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(B) Place the cellulose membrane filter in the filter cassette.

(C) Assemble the sampling train as shown in Figure X-1.

(D) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(E) Adjust the pump rotameter to provide a flowrate of 1 liter/minute.

(F) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (1 in. of Hg).

(G) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to move from one

calibration mark to another. For a 1000-ml buret, a convenient calibration volume is 500 ml.

(H) Repeat the procedure in (G) above at least 2 times, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(I) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, and date and name of the person performing the calibration.

Analytical

(a) Principle of the Method

Sulfuric acid in the air is collected on the cellulose membrane filter and desorbed with distilled water. The pH of the sample solution is adjusted to 2.5 - 4.0 with dilute perchloric acid. After isopropyl alcohol is added bringing the alcohol concentration to approximately 80% by volume, the resulting solution is titrated with 0.005 M barium perchlorate using Thorin [o-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid] as the indicator. The endpoint is determined as a change from yellow to pink.

(b) Range and Sensitivity

The method is sensitive to 0.1 mg sulfuric acid/cu m of air, assuming a 100-liter air sample. The upper limit is the amount of sulfuric acid retained by the filter and is at least 0.5 mg of sulfuric acid.

(c) Interferences

Soluble particulate sulfates in the air sample would give erroneously high sulfuric acid values.

Metal ion interferences can be eliminated by passing the solution through an ion exchange resin.

Concentrations of phosphate and sulfite ions greater than any sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate. Sulfite is corrected for by titration with standard iodine.

(d) Accuracy and Precision

At 1 mg/cu m, the accuracy is at least 10% with a relative standard deviation of 4%. At 10 mg/cu m, the accuracy and relative standard deviation can be improved to about 1%.

(e) Advantages and Disadvantages

The samples are easily collected, stable, and conveniently shipped to the laboratory for analysis.

The analysis is relatively rapid and simple.

A disadvantage is the possible error due to airborne soluble particulate sulfate salts.

(f) Apparatus

- (1) Personal sampling pump with flowmeter capable of sampling at a rate of 1 to 2 liters/minute.
- (2) 37 mm mixed cellulose ester filter, 0.8 μm nominal pore size.
- (3) Necessary glassware.
- (4) A buret of 10-ml capacity graduated in 0.05 ml subdivisions.
- (5) A daylight fluorescent lamp aids in identifying the endpoint.
- (6) Ion exchange columns may be constructed using glass burets or tubing. A column with an inside diameter of 8 mm with 7 inches of resin has a capacity of approximately 25 milliequivalents.

(g) Reagents

- (1) Alcohol-- isopropanol, reagent grade
- (2) Barium perchlorate, 0.005 M-- dissolve 2.0 g of barium perchlorate trihydrate in 200 ml of water and add 800 ml of isopropanol. Adjust pH to about 3.5 with perchloric acid. Standardize against the standard sulfate solution.
- (3) Thorin [o-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid]-- prepare a 0.1-2% solution in distilled water.
- (4) Standard sulfate solution-- prepare a 0.005 M solution of sulfuric acid and standardize by titration with 0.005 M sodium hydroxide

solution or dissolve 0.7393 g anhydrous sodium sulfate in distilled water and dilute to 1 liter (1 ml = 0.5 mg SO₄). The sodium is removed by passage of the standard solution through the ion exchange column.

(5) Hydrochloric acid, 4 N-- add 300 ml concentrated HCl to 600 ml of distilled water. This is needed only to regenerate the column if the ion exchange procedure is used.

(6) Perchloric acid, 1.8%-- dilute 25 ml of reagent grade perchloric acid (70-72%) to 1 liter of distilled water.

(7) Ion exchange resin-- strongly acidic cation exchange resin, 20-50 mesh, or equivalent.

(h) Procedure

(1) Cleaning of equipment-- the glassware should be chemically clean. Wash in detergent and rinse with tap water and distilled water.

(2) Ion exchange procedure (used to purify standard sulfate solution)-- when about two-thirds of the capacity of the resin has been exhausted (deterioration in sharpness of the end point), regenerate the resin by passing 30 ml of 4 N hydrochloric acid through the column. After thorough washing with distilled water, the column is ready for use. Since small volumes of sample solution are passed through the ion exchange column, care must be taken not to dilute the sample with the water that remains on the resin. One way this can be accomplished is by forcing air through

the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or two ml of sample is passed through the column and is discarded after air is again forced through the resin. The remainder of the sample is then passed through the ion exchange column and an aliquot is titrated according to the general procedure in (i)(3) below.

The column is flushed with distilled water between samples to prevent contamination from the previous sample.

(i) Analysis of Samples

(1) Place the filter from the cassette in a filter holder. Desorb the sulfuric acid by passing three 5-ml portions of distilled water through the filter with suction. Dilute the filtrate to a volume of 25 ml.

(2) If air concentrations of metal ions are encountered which exceed that of the sulfate, sample should be passed through the ion exchange column by the procedure detailed in (h)(2) above.

(3) To a 10-ml aliquot, add 40 ml isopropanol. Adjust the pH, if necessary, to between 2.5 and 4.0 with perchloric acid. Add 1 to 3 drops of Thorin indicator and titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the endpoint.

(4) Analyze the standard and reagent blank in the same manner.

(j) Standardization

The barium perchlorate solution is standardized by titrating a 5-ml aliquot with 0.005 M sulfuric acid to the endpoint using Thorin

as indicator. The molarity of the solution is calculated as follows:

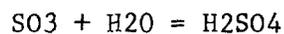
$$M[\text{barium perchlorate}] = \frac{\text{ml}[\text{sulfuric acid}] \times M[\text{sulfuric acid}]}{\text{ml}[\text{barium perchlorate}]}$$

Periodic checks of the molarity of the barium perchlorate solution should be run following this same procedure.

If anhydrous sodium sulfate is used to standardize the barium perchlorate, it must first be ion-exchanged since sodium obscures the endpoint. A 5-ml aliquot of the 0.5 mg/ml sulfate solution is ample for standardization when using a 10-ml buret.

(k) Calculations

The analytical results are calculated on the basis of the following reaction:



$$\frac{\text{mg H}_2\text{SO}_4}{\text{cu m}} = \frac{(A-B) \times C \times E \times 0.510}{D \times F \times G}$$

where

A = ml of sample titrant.

B = ml of reagent blank titrant.

C = ml of standard titrated.

D = ml of standard titrant.

E = volume in ml of sample solution.

F = ml of sample titrated.

G = cu m of air sampled.

0.510 is the product of $\frac{0.5 \text{ mg SO}_4}{1 \text{ ml standard}} \times \frac{\text{H}_2\text{SO}_4 (98.06)}{\text{SO}_4 (96.06)}$

IX. APPENDIX II
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to sulfuric acid shall be provided in the appropriate section of the Material Safety Data Sheet or approved form. If a specific item of information is inapplicable, the initials "n.a." (not applicable) should be inserted.

(a) The product designation in the upper left-hand corner of both front and back to facilitate filing and retrieval. Print in upper case letters in as large a print as possible.

(b) Section I. Source and Nomenclature.

(1) The name, address, and telephone number of the manufacturer or supplier of the product.

(2) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(c) Section II. Hazardous Ingredients.

(1) Chemical or widely recognized common name of all hazardous ingredients.

(2) The approximate percentage by weight or volume (indicate basis) which each hazardous ingredient or the mixture bears

to the whole mixture. This may be indicated as a range of maximum amount, ie, 10-20% by volume; 10% maximum by weight.

(3) Basis for toxicity for each hazardous material such as established OSHA standard in appropriate units and/or LD50, showing amount and mode of exposure and species, or LC50 showing concentration and species.

(d) Section III. Physical Data.

(1) Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure in millimeters of mercury; vapor density of gas or vapor (air=1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water=1); volatility, indicate if by weight or volume, at 70 degrees Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether=1); and appearance and odor.

(e) Section IV. Fire and Explosion Hazard Data.

(1) Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits in percentage by volume in air; suitable extinguishing media or agents; special fire fighting procedures; and unusual fire and explosion hazard information.

(f) Section V. Health Hazard Data.

(1) Toxic level for total compound or mixture, relevant symptoms of exposure, skin and eye irritation properties, principal routes

of absorption, effects of chronic (long-term) exposure, and emergency and first-aid procedures.

(g) Section VI. Reactivity Data.

(1) Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(h) Section VII. Spill or Leak Procedures.

(1) Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers holding residues, contaminated absorbents, etc.

(i) Section VIII. Special Protection Information.

(1) Requirements for personal protective equipment, such as respirators, eye protection, clothing, and ventilation, such as local exhaust (at site of product use or application), general, or other special types.

(j) Section IX. Special Precautions.

(1) Any other general precautionary information such as personal protective equipment for exposure to the thermal decomposition products listed in Section VI, and to particulates formed by abrading a dry coating, such as by a power sanding disc.

(k) The signature of the responsible person filling out the data sheet, his address, and the date on which it is filled out.

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing,
Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME		EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, and ZIP Code)		
CHEMICAL NAME AND SYNONYMS		TRADE NAME AND SYNONYMS
CHEMICAL FAMILY	FORMULA	

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					
HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	TLV (Units)

SECTION III - PHYSICAL DATA

BOILING POINT (°F.)		SPECIFIC GRAVITY (H ₂ O=1)	
VAPOR PRESSURE (mm Hg.)		PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_____ =1)	
SOLUBILITY IN WATER			
APPEARANCE AND ODOR			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	Uel
EXTINGUISHING MEDIA			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARDS			

SECTION V - HEALTH HAZARD DATA	
THRESHOLD LIMIT VALUE	
EFFECTS OF OVEREXPOSURE	
EMERGENCY AND FIRST AID PROCEDURES	

SECTION VI - REACTIVITY DATA			
STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE		
INCOMPATIBILITY <i>(Materials to avoid)</i>			
HAZARDOUS DECOMPOSITION PRODUCTS			
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR		

SECTION VII - SPILL OR LEAK PROCEDURES	
STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED	
WASTE DISPOSAL METHOD	

SECTION VIII - SPECIAL PROTECTION INFORMATION			
RESPIRATORY PROTECTION <i>(Specify type)</i>			
VENTILATION	LOCAL EXHAUST	SPECIAL	
	MECHANICAL <i>(General)</i>	OTHER	
PROTECTIVE GLOVES		EYE PROTECTION	
OTHER PROTECTIVE EQUIPMENT			

SECTION IX - SPECIAL PRECAUTIONS	
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	
OTHER PRECAUTIONS	

Table X-1

STRENGTHS, PROPERTIES, AND CHARACTERISTICS
OF SULFURIC ACID AND OLEUM

I. Strengths

Sulfuric Acid

Degrees Baume'	% H ₂ SO ₄	Sp G at 60 F Compared to H ₂ O/60 F	Freezing Point	
			C	F
52	65.13	1.5591	-40.0	-40
58	74.36	1.6667	-44.0	-47
60	77.67	1.7059	- 8.0	18
66	93.19	1.8354	-32.0	-26
—	98.00	1.8438	3.0	37
—	100.00	1.8392	10.0	50

Oleums

% Free SO ₃	% Equivalent H ₂ SO ₄	Sp G at 100 F Compared to H ₂ O/60 F	Freezing Point	
			C	F
20.0	104.50	1.8820	- 9.0	15
30.0	106.75	1.9156	15.5	60
40.0	109.00	1.9473	33.0	94
65.0	114.63	1.9820	3.6	34
100.0 (Liquid SO ₃)	122.50	1.8342	17.2	63

II. Properties and Characteristics

Physical state	Liquid
Color	Clear, colorless to cloudy
Odor	Oleum has a sharp, penetrating odor
Flash point	None
Corrosivity	Highly corrosive to most metals, particularly at concentrations below 60 Be with evolution of hydrogen gas.
Reactivity	In addition to attacking many metals, the acid in its concentrated form is a strong oxidizing agent and may cause ignition on contact with organic materials and such products as nitrates, carbides, chlorates, etc. It also reacts exothermically with water.
Hygroscopicity	Yes

Derived from [3]

Table X-2

END USES OF SULFURIC ACID

Phosphatic fertilizers	Regenerated cellulose sheet film (chiefly cellophane)
Petroleum products	Dyes
aviation gasoline	Insecticides
catalysts	Rubber, including synthetic
sulfonates (lube oil additives)	Hydrochloric acid
Ammonium sulfate	Chromium chemicals
synthetic	Light oil refining
coke-oven	Storage batteries
Inorganic pigments	Tall oil
Iron and steel	Chlorine drying
Alcohols	Industrial water treatment
Rayon	Medicinals
high-tenacity yarn	Textile finishing
Aluminum sulfate	Copper sulfate
water and sewage treatment	Fat-splitting
Nonferrous metallurgy	Sulfonated oil
Industrial explosives	
Synthetic detergents	

Derived from [5]

Table X-3

OCCUPATIONS CONSIDERED TO FREQUENTLY
INCLUDE EXPOSURES TO SULFURIC ACID

aluminum sulfate makers	laboratory workers, chemical
ammonium sulfate makers	metal cleaners
battery maker, storage	paint makers
cellulose workers	paper makers
copper sulfate makers	petrochemical workers
detergent makers	petroleum refinery workers
drug makers	phenol makers
dye makers	phosphate workers
electroplaters	phosphoric acid makers
explosive makers	pigment makers
fertilizer makers	rayon workers
food processors	rubber workers
fur processors	steel workers
galvanizers	sulfuric acid workers
glue makers	textile workers
jewelers	

Derived from [6]

TABLE X-4
DISTRIBUTION OF AIRBORNE SULFURIC ACID CONCENTRATIONS

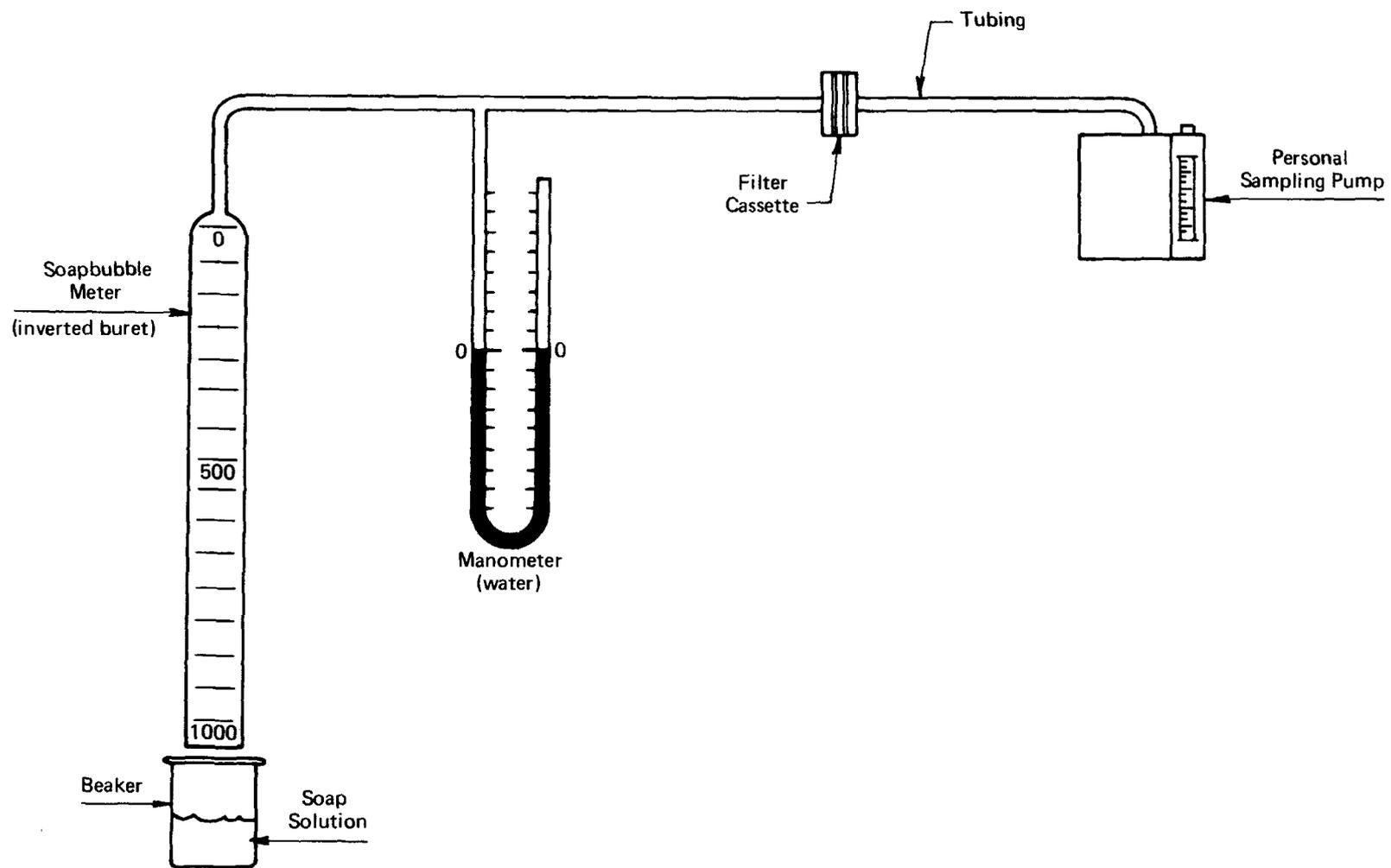
Dept.	Number of times sulfuric acid concentration observed ($\mu\text{g}/\text{cu m}$)									Total No. of Observations
	0-499	500-999	1000-1499	1500-1999	2000-2999	3000-3999	4000-4999	5000-9999	10000 and over	
A	41 (248)*	5 (676)	2 (1205)	- -	- -	- -	- -	- -	- -	48 (333)
B	19 (277)	10 (746)	4 (1292)	8 (1729)	1 (2626)	- -	- -	- -	- -	42 (795)
C	15 (360)	21 (718)	13 (1187)	4 (1753)	7 (2412)	4 (3427)	4 (4441)	11 (6704)	6 (14433)	85 (2960)
D	10 (183)	10 (791)	10 (1228)	1 (1751)	1 (2462)	3 (3560)	1 (4291)	2 (5618)	- -	38 (1380)
E	3 (221)	6 (755)	1 (1395)	1 (1551)	- -	1 (3517)	- -	- -	- -	12 (971)
Total No. of Observations	88	52	30	14	9	8	5	13	6	225

*Mean concentrations for each cell are shown in parentheses.

Derived from [29]

FIGURE X-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE AND FILTER



74-128 H₂SO₄